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Wolter et al.

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(54) **HYDROLYSABLE AND POLYMERIZABLE
SILANES WITH ADJUSTABLE SPATIAL
DISTRIBUTION OF THE FUNCTIONAL
GROUPS, AND USE THEREOF**

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See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,627,806 A * 12/1971 LeGrow 556/427
4,429,082 A 1/1984 Lee et al.
4,652,610 A 3/1987 Dowbenko et al.
4,652,664 A * 3/1987 Singer et al. 556/427
4,687,709 A 8/1987 Brinkmeyer et al.
4,720,534 A * 1/1988 Singer et al. 528/28

4,777,233 A * 10/1988 Suzuki et al. 528/32
5,091,440 A * 2/1992 Griswold 522/99
5,233,006 A * 8/1993 Wolter et al. 528/32
5,412,133 A * 5/1995 Eckberg 556/427
5,532,398 A * 7/1996 Wolter et al. 556/420
5,919,885 A * 7/1999 Wolter et al. 528/32
6,124,491 A 9/2000 Wolter et al.

(Continued)

FOREIGN PATENT DOCUMENTS

DE 10349766 A1 6/2005
DE 102008059129 A1 5/2010

OTHER PUBLICATIONS

T. E. Müller et al.: "Hydroamination: Direct Addition of Amines to
Alkenes and Alkynes", Chem. Rev. 2008, 108, 3795-3892.

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(57) **ABSTRACT**

The present invention relates to a process for a chain extension
of radicals bonded to silicon via carbon in silanes or
siloxanes while maintaining or increasing the number of
functional groups on the respective Si—C-bonded radicals,
wherein a silane or siloxane with a radical bonded to a silicon
atom by a carbon atom, which bears at least two functional
groups, wherein a first group of the functional groups is an
unsaturated, organically polymerizable group and a second
group of the functional groups is selected from among

(a) additional unsaturated, organically polymerizable groups,
(b) COOR⁸ or —(O)_bP(O)(R⁵)₂ and (c) —OH,
with R⁸ equal to R⁴ or M_{1/x}^{x+} wherein M^{x+} is a hydrogen or an
x-fold positively charged metal cation, and b=0 or 1,
is converted in a first reaction with a compound of a formula
(I)



wherein

X is SH, NH₂ or NHR⁴, Z is OH, the carboxylic acid radical
—COOH or a salt or an ester of this radical or a silyl
radical, W is a substituted or non-substituted hydrocarbon,
the chain of which can be interrupted by —S—, —O—,
—NH—, —NR⁴—, —C(O)O—, —NHC(O)—, —C(O)
NH—, —NHC(O)O—, —C(O)NHC(O)—, —NHC(O)
NH—, —S(O)—, —C(S)O—, —C(S)NH—, —NHC
(S)—, —NHC(S)O—, and a is 1, 2, 3, 4 or a greater whole
number,

wherein R⁴ is a non-substituted or substituted hydrocarbon
radical,

R⁵ is a non-substituted or substituted hydrocarbon radical or
OR⁶,

R⁶ is hydrogen or a non-substituted or substituted hydrocar-
bon radical to such an extent that the radical X connects to
the first functional group.

19 Claims, No Drawings

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References Cited

U.S. PATENT DOCUMENTS

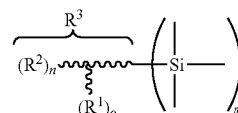
6,794,527 B1 9/2004 Wolter et al.
7,977,404 B2* 7/2011 Wolter et al. 523/116
2008/0187499 A1 8/2008 Wolter et al.

2009/0023883 A1 1/2009 Wolter
2010/0184880 A1 7/2010 Fukui
2011/0082250 A1 4/2011 Wolter
2014/0088279 A1 3/2014 Wolter et al.

* cited by examiner

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It may also be preferred to bond additional functional groups to the silicon-bonded radical throughout the course of such movements. Additional groups, such as hydroxy groups or acid groups, can positively influence the matrix hydrophilicity or other properties of the condensates, polymers, and composites produced from the silanes. Furthermore, this allows for the simultaneous formation of a dendrimer-like structure on a carbonaceous radical upon repeated execution of the extension reactions.



If a structure (1) represents a silane, the three bonds of the Si atom not further identified stand for additional radicals bonded to a silicon atom. Instead, they can symbolize oxygen bridges to additional silicon atoms or other metal atoms if said structure (1) is a component of a silicic acid (hetero) polycondensates. (The expression “(hetero) polycondensates” means that the condensate, in addition to silicon, may have other metal atoms of co-condensed compounds, for example, B, Al, Ti, Zn, and/or additional transition metal atoms). Due to the fact that the reactions relevant to the invention can occur on monomeric silanes as well as on inorganically linked silicic acid polycondensates, the nature this bond is not essen-

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tial. In the case of monomeric silanes, these radicals, for instance under hydrolysis conditions, can be hydrolysable groups, as they are referred to by specialists, for example, halogenides or alkoxides. Instead, one or more of these groups can represent OH. In other embodiments, at least one radical of the bond symbolizes at least one additional radical bonded to the silicon atom by carbon, which can have any number of properties. They can deviate from those of radical R³; alternatively one or even two such radicals can have the meaning of R³.

The indices m and n stand independently from each other for 1 or 2, though potentially for 3, 4 or even greater. Frequently, m and n are respectively 1, wherein, however, in some cases n may mean 2, 3, or even 4. Theoretically, there is no upward limitation.

The index o is highly variable and, in the case of silicic acid condensates, does not have to represent a whole number. It should preferably be at least 0.2 and is frequently between 0.5 and 1.0. However, it can also be greater than 1, e.g. 1.5 or 2.0, or even higher. If the index o is not a whole number, i.e. not every radical R³ in the polycondensate has one (or more) radicals R¹, said radicals R³, which are free from R¹ or do not have the maximum number thereof, instead generally have those substituents, from which R¹ was previously formed. This can likewise be reactive, although it does not play any further role then in the scope of the invention (see e.g. the second example of the first reaction shown further below).

The branching of the hydrocarbon backbone depicted in formula (1) shown with the diverging zigzag line is optional. In specific embodiments, radical R¹ can namely be a substituent, which is directly bonded to an atom of the backbone of R³. One example is the case, wherein R¹ represents group CHR'=CH—C(O), which is bonded directly to a nitrogen atom (N*) from the backbone of the Si—C bonded radical (symbolized by both bonds on the nitrogen pointing to the right) in the form of a (meth)acrylic acid amide (CHR'=CH—C(O)—N*—). In this case, R¹ can mean, e.g. hydrogen or CH₃.

Examples of structures capable of being used pursuant to an invention (1) are:

Silanes of a General Formula (A):



wherein the radicals have the following meaning:

X: hydroxy, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl or —NR''₂;

R: alkyl, alkenyl, aryl, alkylaryl or arylalkyl;

R': alkylene, arylene or alkylarylene;

R'': hydrogen, alkyl or aryl;

A: O, S, PR'', POR'' or NHC(O)O;

B: straight-chain or branched out organic radical that is derived from a compound with at least three C=C double bonds and 5 to 50 carbon atoms;

a: 1, 2 or 3;

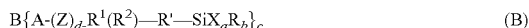
b: 0, 1 or 2;

c: 0 or 1;

x: whole number, the maximum value of which corresponds to the number of double bonds in is the compound B minus 1,

as well as silicic acid polycondensates derived thereof formed by hydrolytic condensation of the silanes of formula (A). Such silanes and polycondensates are revealed in DE 40 11 044 A1. They fall under present structural formula (1) with R¹ and R² equal to an organically polymerizable radical.

Silanes of a General Formula (B):



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wherein the radicals and indices have the following meaning:
A=O, S, NH or C(O)O;

B=straight-chain or branched out organic radical that is derived from a compound with at least one C=C double bond and 4 to 50 carbon atoms;

R=alkyl, alkenyl, aryl, alkylaryl or arylalkyl;

R'=alkylene, arylene, arylalkylene or alkylarylene with respectively 0 to 10 carbon atoms, wherein these radicals can be interrupted by oxygen and sulfur atoms or by amino groups;

R¹=nitrogen, alkylene, arylene or alkylarylene with respectively 1 to 10 carbon atoms, wherein these radicals can be interrupted by oxygen or sulfur atoms or by amino groups;

R²=OH or COOH;

X=hydroxy, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl or —NR''₂;

R''=alkyl or aryl;

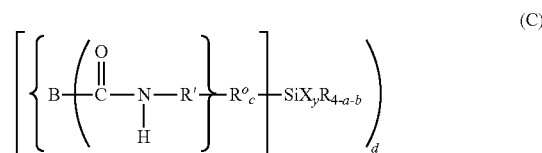
Z=CO or CHR, with R equal to H, alkyl, aryl or alkylaryl;

a=1, 2 or 3;

b=0, 1 or 2;

as well as silicic acid polycondensates derived thereof and formed by hydrolytic condensation of the silanes with formula (B). Such silanes and silicic acid polycondensates are revealed in DE 44 16 857 C1. They represent the structures of formula (1), wherein R² is a hydroxy group or a carboxylic acid group.

Silanes of a General Formula (C)



wherein the radicals and indices have the following meaning:

B=organic radical with at least one C=C double bond;

R=alkyl, alkenyl, aryl, alkylaryl or arylalkyl;

R^o and R' respectively=alkylene, alkenylene, arylene, alkylarylene or arylalkylene;

X=hydroxy, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl or —NR''₂ with R'' equal to hydrogen, alkyl or aryl;

a=1, 2 or 3

b=1, 2 or 3, with a+b=2, 3 or 4;

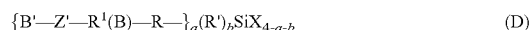
c=1;

d=1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

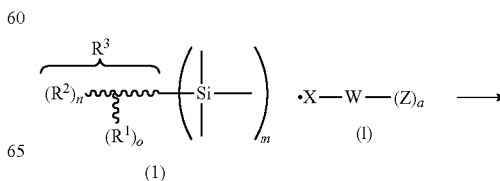
e=2 or 3 or 4;

as well as silicic acid polycondensates derived thereof and formed by hydrolytic condensation of the silanes of formula (C). Said silanes of formula (C) and the silicic acid polycondensates capable of being derived thereof are revealed in DE 199 10 895 A1. They fall under the structures of formula (1), in which R² is an organically polymerizable radical. In the case that b represents 2 or 3 in formula (C), one or two of the additional bonds of the silicon atom have the meaning of R³ in formula (1)

Silanes of a General Formula (D):



wherein the radicals and indices have the following meaning:
R is an alkylene, arylene or alkylarylene group, which can be interrupted by one or more oxygen or sulfur atoms or carboxyl or amino groups, or can carry such atoms/groups on its end facing away from the silicon atom;

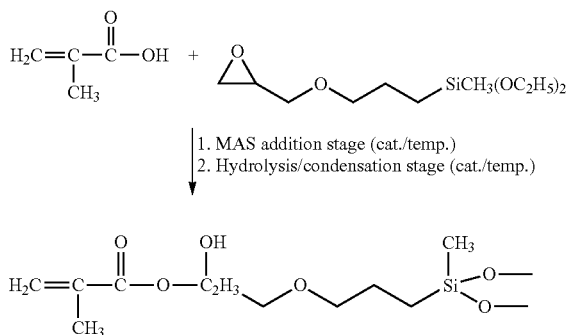


$$\begin{array}{c} \text{R}^3 \\ | \\ (\text{R}^2)_n - \text{Si} - \left(\text{Si} \right)_m \\ | \\ (\text{AW(Z)}_a)_o \end{array} \quad (2)$$

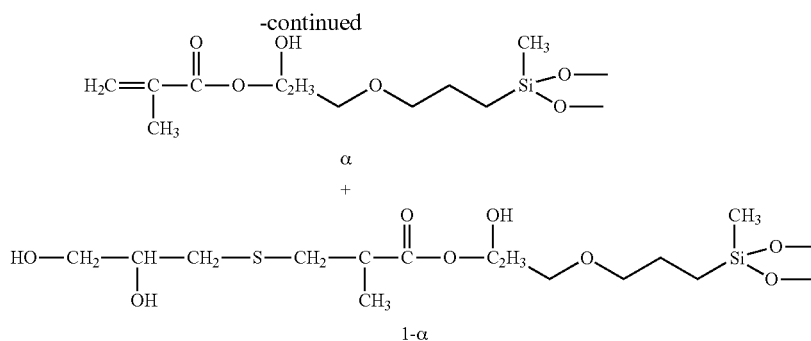
In one preferred embodiment independent thereof, which can be combined with each of the previously mentioned

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As an output material, a silicic acid polycondensate is used in the first of these examples as structure (1), which was produced through hydrolysis and condensation of a silane of general formula (B) (preferably in the "Sol-Gel" process):


$$\begin{array}{c}
 \text{H}_2\text{C}=\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{C} \end{array} \text{O}-\text{C}_2\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{CH}_2-\text{Si} \begin{array}{l} \text{CH}_3 \\ \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \\
 \text{CH}_3 \\
 \text{1}
 \end{array}
 +
 \begin{array}{c}
 \text{HS}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{OH} \\
 \text{OH} \\
 \text{1-}\alpha
 \end{array}$$

$\downarrow \text{+/- Cat.}$



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The product of this reaction (application examples 1a and 1b) contains a radical R^3 extended by one sulfur atom and three carbon atoms, in which the original functional group (the organically polymerizable group) is replaced by a hydroxy group. Furthermore, the product contains an additional hydroxy group. It contains one thioether group as a linkage group A.

Instead of a compound with formula (I), in which X is a mercapto group, this reaction could also be conducted with a compound of formula (I), in which X is a primary or, less preferred, a secondary amino group. With regard to the chain extension highlighted by the invention, the selection of radical X does not play a role, as it is only responsible for the structure of linkage group A between the newly linked radical —W—Z and the radical molecule, which—with a single exception—has no technical function or effect. This exception involves the mercapto group, the use of which as radical X offers a specific benefit—the integration of the sulfur atom as a linkage group A in the makeup of the Si—C bonded radical causes an increase of the refractive index n_D of the formed silicic acid polycondensate compared to a secondary or tertiary amino group.

Instead of a diol used in the example for the compound of formula (I), mono-alcohols may naturally be used as well; in this case, the additional introduction of hydroxy groups is omitted. Alternatively, compounds with more than two hydroxy groups may also be used as a compound of formula (I).

In another variation of the invention, a compound of formula (I) is used for the initial reaction, in which the radical Z represents a silyl group or a carboxylic acid radical (CO_2H) or an ester or a metallic salt of said carboxylic acid radical. Even mixed compounds are possible, i.e. those compounds that have a hydroxy as well as an acidic function.

Specific examples for compounds of formula (I) are:

Thiols functionalized with OH having only one hydroxy group, such as:

- 6-Mercapto-1-hexanol,
- 4-(Mercaptohexyloxy)-benzyl alcohol,
- 2- or 3- or 4-Mercaptophenol,
- 11-Mercapto-1-undecanol,
- 1-Mercaptoundec-11-yl)-tetraethylene glycol.

Thiols functionalized with CO_2H :

- 11-Mercaptoundecanoic acid
- 3-Mercaptopropionic acid
- 3- or 4-Mercaptophenyl acetic acid
- 16-Mercaptohexadecanoic acid
- 6-Mercaptocotinic acid
- 8-Mercaptooctanoic acid
- 15-Mercaptopentadecanoic acid
- 4-Mercaptophenyl acetic acid

Mercaptosuccinic acid

Thiols functionalized with a silyl radical:

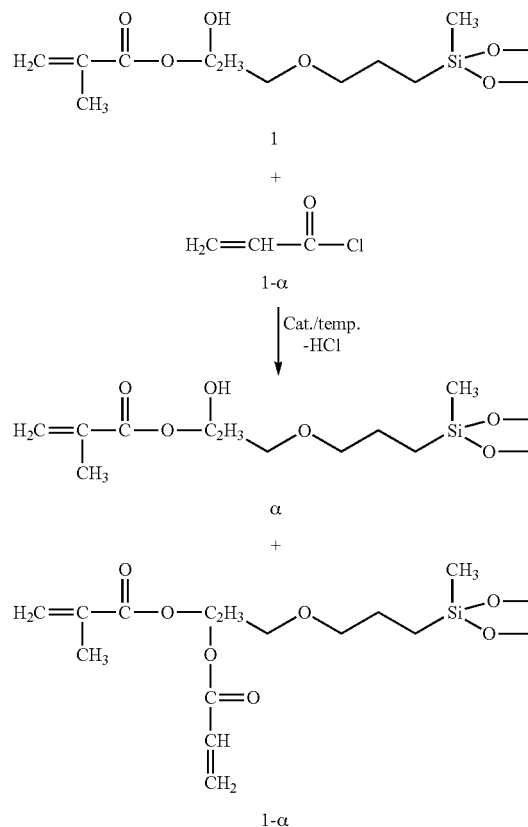
3-Mercaptopropyltrimethoxysilane,

3-Mercaptopropyltriethoxysilane,

3-Mercaptopropylmethyldimethoxysilane.

If Z in compound (I) is a silyl radical, groups are introduced, which permit an additional inorganic hydrolysis and condensation.

A silicic acid polycondensate serves as an output material in a second example of the initial reaction, which was produced through hydrolytic condensation of a silane of general formula (D):

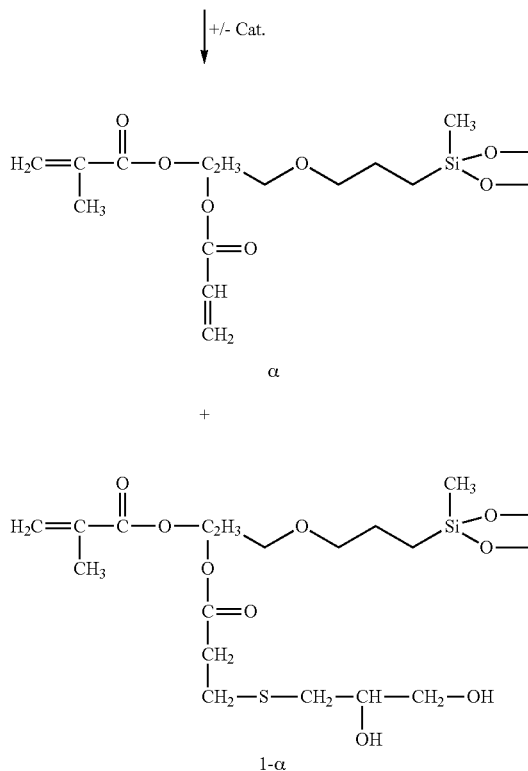
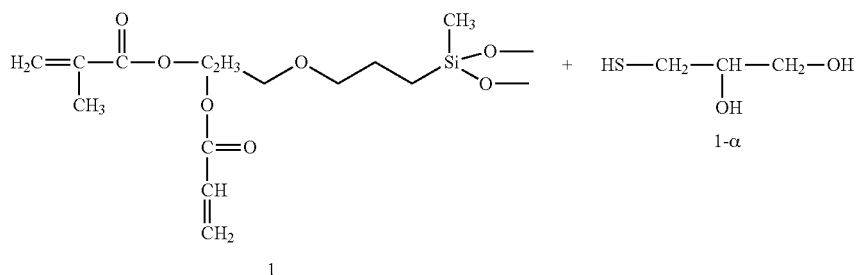


This structure is designated as “Base Resin II” in the following. Noteworthy here is that this polycondensate contains two different structures of formula (1), in which in one case R^1 represents an unsaturated, organically polymerizable group and OH in another, as the underlying reaction was

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conducted with a deficit of acrylic acid chloride. Mixed output materials of this type can be used as needed just as incompletely reacted (i.e. those with $\alpha < 1$) present in all variations. In this regard, a ratio is potentially preferably used of 0.6 to 0.95 mol of the reagent introducing radical R^1 , e.g. 0.6 to 0.95 mol of acrylic acid chloride per mol of hydroxy group for the introduction of an acrylate group is used as R^1 ; instead of this, however, the acrylic acid compound can naturally also be used as needed up to molar equivalence or, in some case, even beyond. However, the latter is frequently unbeneficial with respect to the desire to prevent the presence of monomer radicals in a resin.

The structure with formula (D) is then converted with a compound of formula (I) in this second example as well, X being a mercapto group, Z being a hydroxy group, W being a saturated hydrocarbon group with three carbon atoms, and $\alpha = 2$:



In this example, both R^1 and R^2 are each unsaturated, organically polymerizable groups; however, they differ from each other. The reaction with compound (I) has been selected in the process in such a manner that SH is preferably added to the acrylate group and not to the methacrylate group. Thus,

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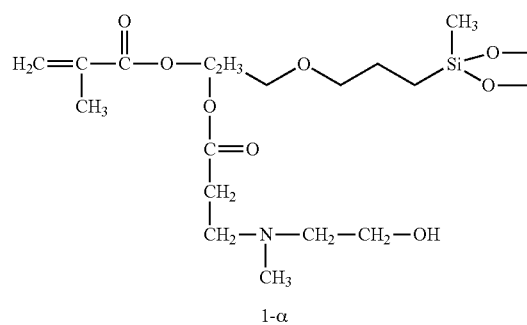
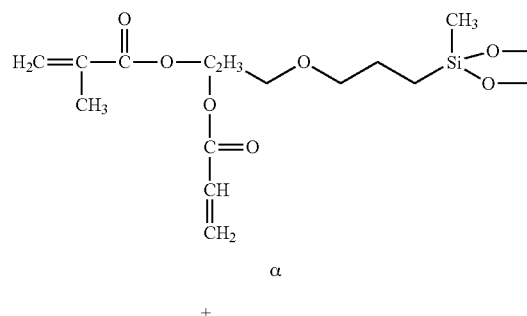
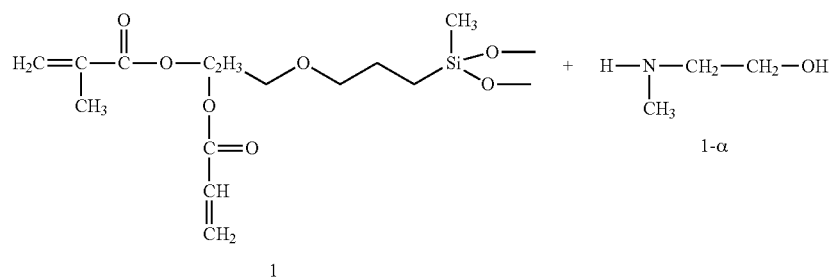
the reaction is stereospecific—the acrylate radical is extended. Due to the addition of thiol, we can observe a drastic increase of polarity/hydrophilicity as a result of the increase of the OH content and—surprisingly—an extremely high deflection to the point of breakage after the hardening, while the breaking strength and the modulus of elasticity are decreased (see also Example 5a).

With regard to the possible variation of this exemplary reaction through the use of other compounds of formula (I) Instead of 3-Mercaptopropan-1,2-diol, it is necessary to refer to the entire explanation for the first example. Naturally, all specified compound types or specific examples for compound (I), which were mentioned for the first reaction in conjunction with the explanation for the first example, can be used for this reaction in combination with the second example.

As an example for a compound (I), in which X is an amino group, the reaction of the structure with formula (D), as it was previously demonstrated for the second example, is represented with a hydroxy-substituted, secondary amine (third example of the first reaction):

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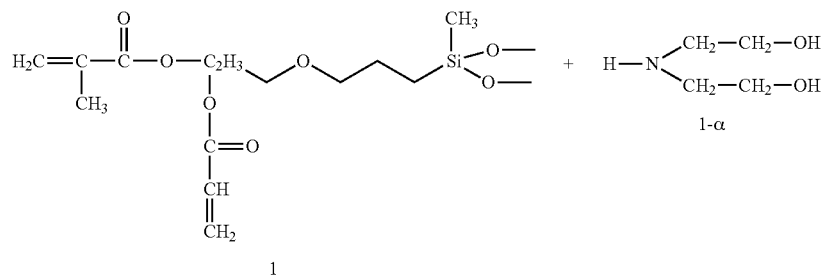
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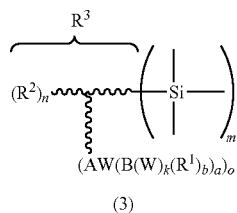
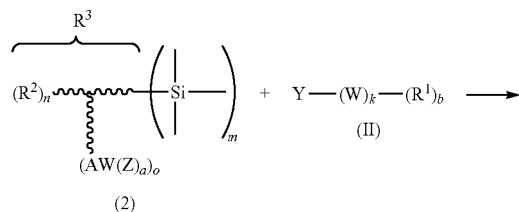
The difference to the previous example is only in the type of linkage group (in this case a tertiary amine instead of a thioether bridge), which, as explained above, is functionally inessential (although the refractive index can be varied by the provisioning or omission of the thioether group), the use of a molecule that is shorter by one CH₂ group and by the presence

of only one hydroxy group (α=1) (see also application example 7a).

Even with this reaction, α cannot only represent 1, but rather 2 instead (or potentially 3 or 4 or more), as the following example shows:



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In the process, the compound (II) can carry multiple radicals R^1 (i.e. b can be 1, 2 or even greater), such that the number of double bonds per Si—C-bonded radical can be increased. In combination with a first reaction, for which the compound (I) carries two or even more radicals Z , a dendrimer-like structure of this type can be applied.

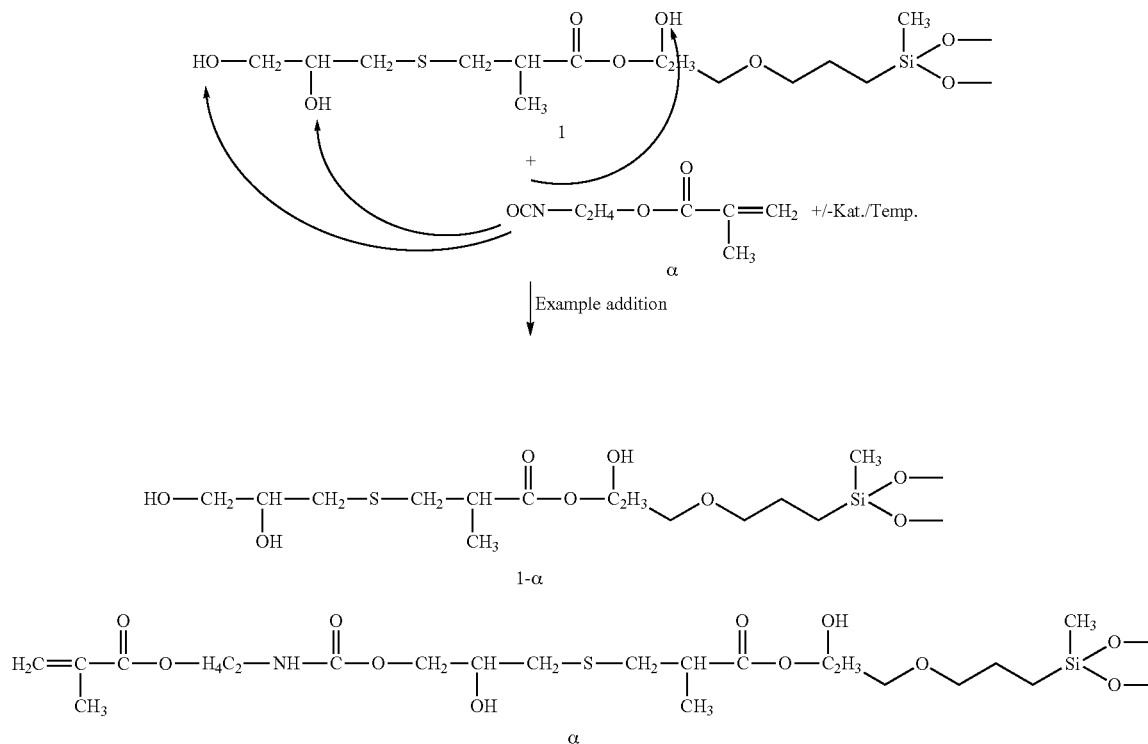
Thus, the product of the first variation of the second reaction is in turn a compound or a condensate with at least one

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radical R^1 and at least one radical R^2 on the Si—C-bonded radical R^3 , wherein, however, the radical R^1 is distanced from the silicon atom with respect to radical R^1 in the output material, which is extended through both reactions by A—W—B—W— and is present b times a -fold with respect to the original number o in the output material. The presence of a greater number of double bonds that can move relatively well across longer chains, which are essentially located in the outer area of the silane molecule or the siloxane, can lead to a decrease of the contraction for subsequent cross-linking, which can be particularly advantageous in the dental field. Furthermore, the radical of R^3 can potentially have additional functionalities, e.g. through the use of a compound of formula (I), which has at least two hydroxy groups, and/or a compound of formula (II), which has more than one unsaturated, organically polymerizable radical.

The first variation of the second reaction is explained in further detail in the following on the basis of examples. The first of these two examples are based on the product of the first example above for the first reaction; the third example is based on the product of the second example above for the first reaction:

The First Example for the Second Reaction (Reaction of a Compound Containing a Hydroxy Group with one Isocyanate, in this Case, an Isocyanate (Meth)Acrylate (Variation 1)



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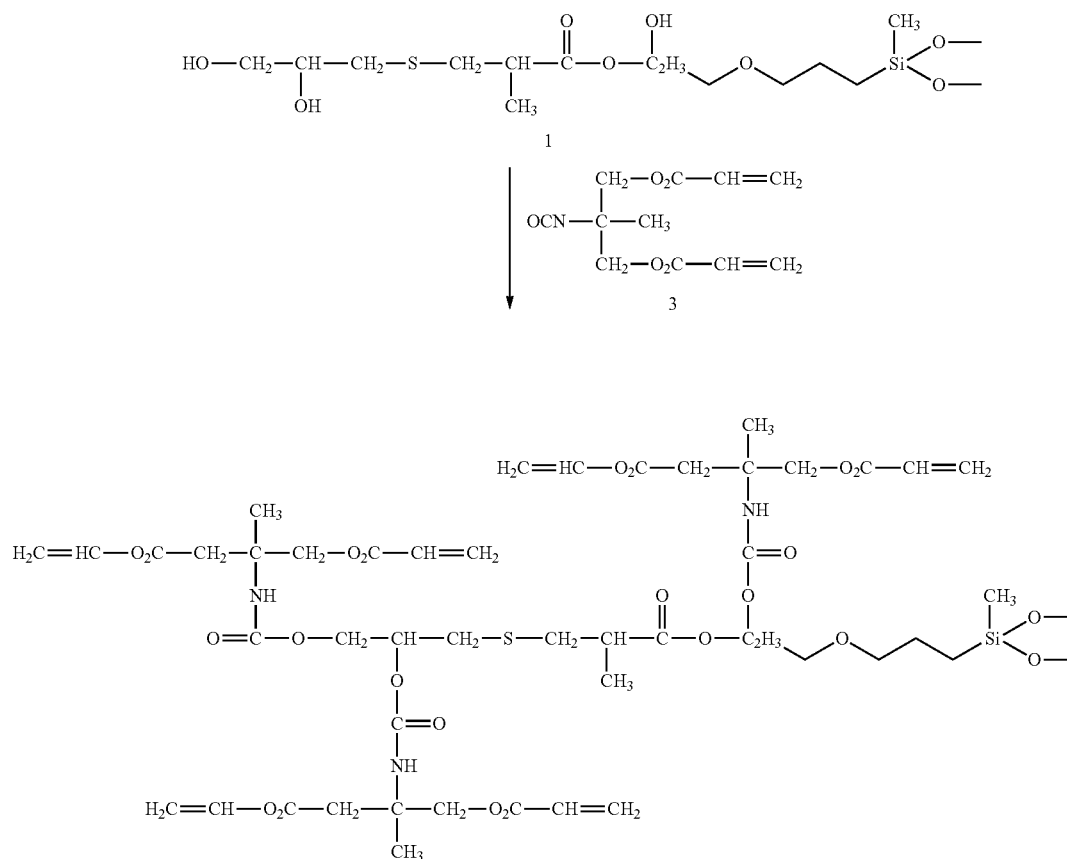
The product is identified with (3-1). The preferred, though not exclusive, point of connection of the isocyanate-methacrylate as a compound (II) is the primary hydroxy group on the Si—C-bonded radical. Thus, a mixture arises with a primarily silyl-methacrylate structure, in which the methacrylate group was shifted outward by the group $\text{H}_4\text{C}_2\text{NH—C}(\text{O})\text{—O—CH}_2\text{—CH}(\text{OH})\text{—CH}_2\text{—S}$ with respect to those of the output compound (1). Due to the fact that the output material for this reaction does not have to be the pure reaction product of the first reaction, but rather can be present in the mixture with unreacted material of the first reaction, a finely graded spectrum of products with strong, but varyingly improved physical properties, such as breaking strength, modulus of elasticity or deflection, can be produced, while surprisingly the hardening shrinkage does not further increase (see Application example 2b to 2e with the respective values for these parameters).

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reacted secondary hydroxy group arises or an Si—C-bonded radical with three methacrylate groups.

If the reaction occurs, for example, with three mol of compound (II) (i.e. $\alpha=3$ in the upper formula scheme), we obtain a product with the structure (3), wherein all three hydroxy groups are replaced by methacrylate groups. Based on a structure having one C=C double bond and one hydroxy group as the two functional groups of the output material, we will thus achieve, e.g. structures with three methacrylate groups laying far from each other, which respectively hang on the lateral chains of the Si—C-bonded radical (the reaction scheme is depicted further below; Structure 3-2) through combination of the first and second reaction.

Naturally, the first variation of the second reaction can also be conducted with compounds (II), in which b is greater than 1. One example for a reaction (II) with b=2 is shown in the following, which identifies the resulting structure with (3-3):

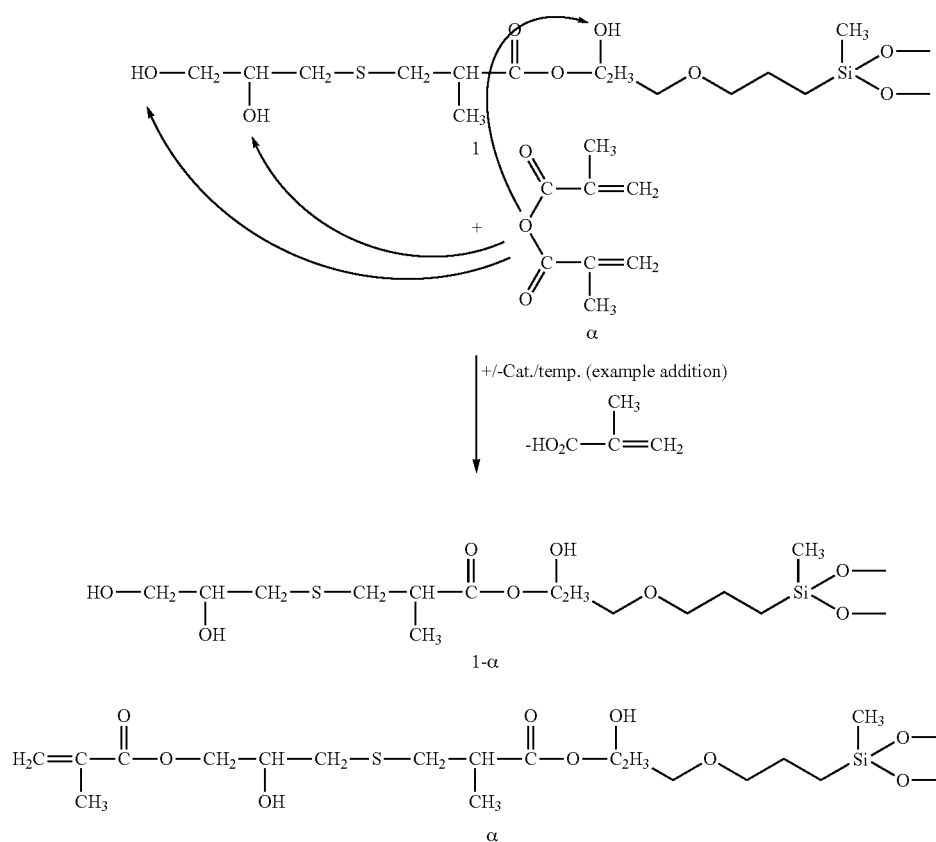


In this example on the other hand, a deficit on the compound (II) can be used so that a part of the output material remains unreacted, as was described above for the first reaction (see Example 6a). In this example, however, more than one molar equivalent (III) can also be used instead due to the fact that overall three hydroxy groups are present on the Si—C-bonded radical, which can potentially react with the isocyanate (II) as well, see Application example 6b. Depending on the amount of compound (II) used, which can be up to 3 molar equivalents, either a mixture having a partially

The original radical R^2 is likewise converted in this structure (3-3) and therefore changed its meaning with respect to the definition in structure (1) to $\text{B—(W)}_k\text{—(R}^1\text{)}_b$. This is naturally also true for all comparable reactions—if R^2 in a structure (2) represents Z (equal or different than the remaining groups Z of structure (2)), this radical can generally be involved in the following reactions and for its part contribute to the outward shifting of radicals or dendrimerization.

The reactions occur analogously if a reactant carries groups containing carboxyl groups instead of hydroxy groups; this results in acid amide groups.

Second Example for the Second Reaction (Variation 1):

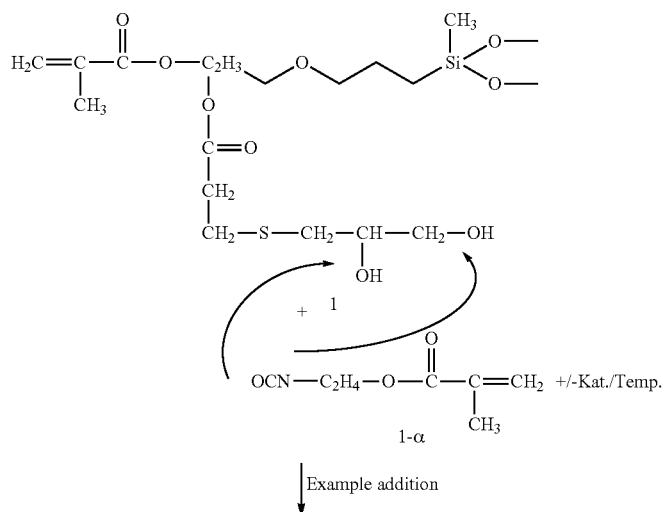


This example differs from the previous in that instead of an isocyanate, an anhydride (in this case the anhydride of methacrylic acid) is used; the product is shorter than that of the first example for this reaction by one ethyl urethane unit. The same product could be achieved with another activated methacrylic acid, e.g. with methacrylic acid chloride. In this case, an

extreme increase of the strength and modulus of elasticity was able to be observed as well (see also Application example 3).

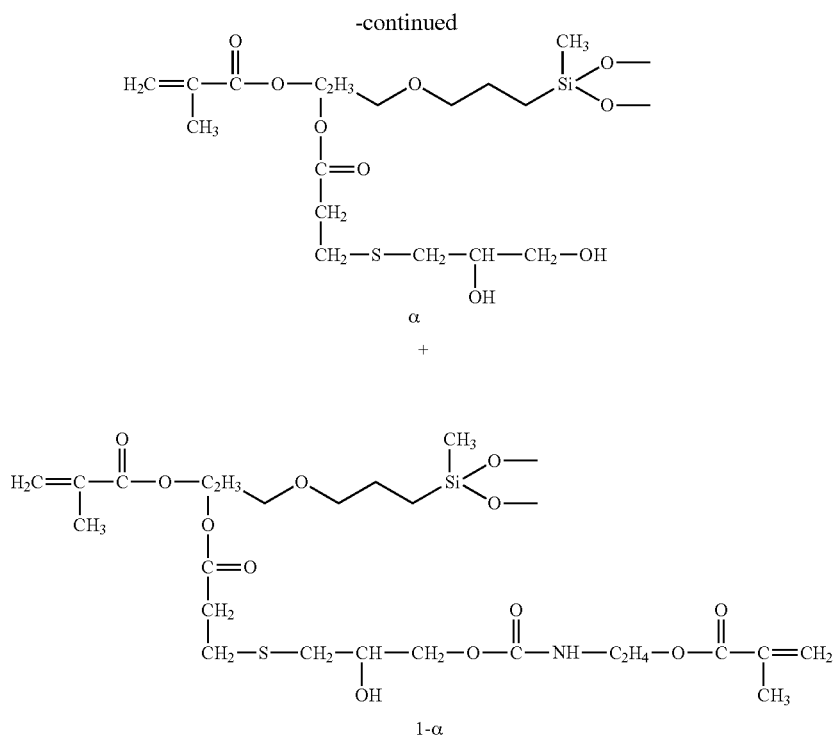
With regard to the molar ratios, the same applies respectively as described for the previous example.

Third Example for the Second Reaction (Variation 1):



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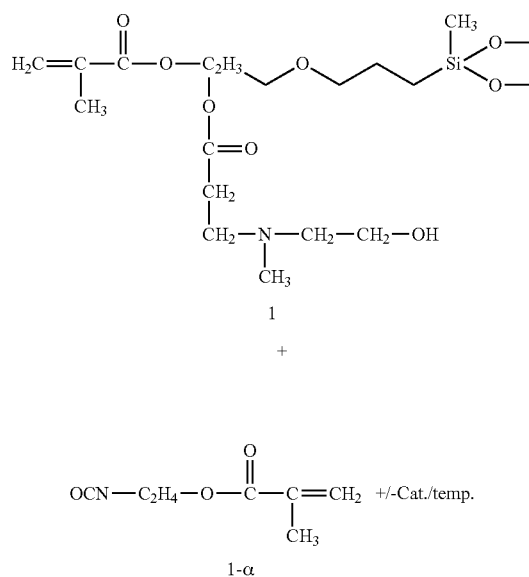


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Even in this case, either (barely) a mol of isocyanate of formula (II) or up to two mol of isocyanate can be used; accordingly one product is obtained, for which the methacrylate group is clearly shifted outward compared to the output material, and that carries either a second methacrylate group or an additional hydroxy group. With respect to the latter variation, it is necessary to note the application examples 6a and 6b—the addition of an isocyanate methacrylate leads to

an extreme increase of the breaking strength of the modulus of elasticity with a high degree of deflection.

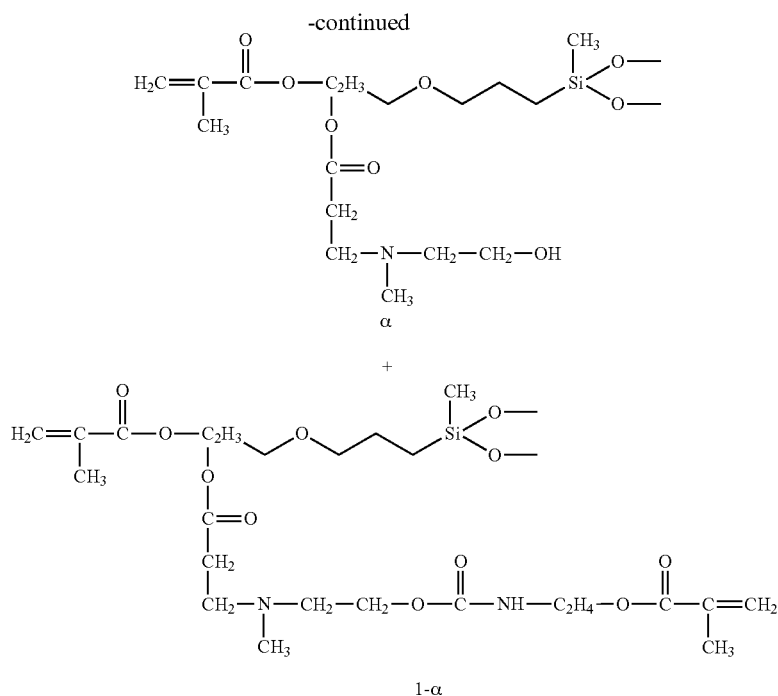
Instead of a product of the first reaction, which was obtained through the reaction with a mercapto compound, for example, a product achieved with an amine may be used as output material, e.g. the above shown product of the reaction of a structure with formula (D) with a hydroxylamine, which was reacted in this case with Isocyanate methacrylate.



↓ Example addition

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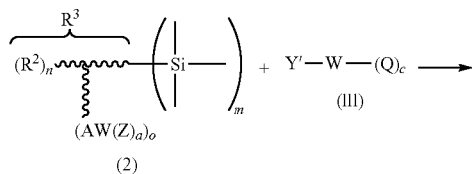


If the product with Di(2-hydroxyethyl)amine is used instead of that of the reaction of the above shown structure with formula (D), a mixture is achieved, see, e.g. Application example 10a. Depending on the amount of compound (I) or compound (II) used relative to the base resin, the properties of the product will vary—see Application example 8a to 8c.

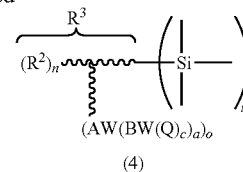
The products (3) of the first variation of the second reaction contain double bonded organically polymerizable groups, which are arranged at a greater distance to the Si atom on the Si—C-bonded radicals compared to the output material. This is one objective of the present invention. They can continue to be used in this form.

In a further development of the invention, however, they can in turn serve as output material for an additional cycle from the first and potentially second reaction. As a result, they allow the unsaturated, organically polymerizable groups to be shifted even further outward, etc.; instead of this, products with additional reactive groups can be obtained as described above. If additional functional groups are introduced in the process, which can be likewise connected to the above described reactions, we will obtain dendrimer-like structures. Before we explain this in further detail, however, the second variation of the second reaction is depicted:

In the second variation of the second reaction, the silane or the silicic acid polycondensate with the structure (2), wherein Z=OH or COOH or a carboxylic acid salt, is converted with a compound of formula (III):



-continued



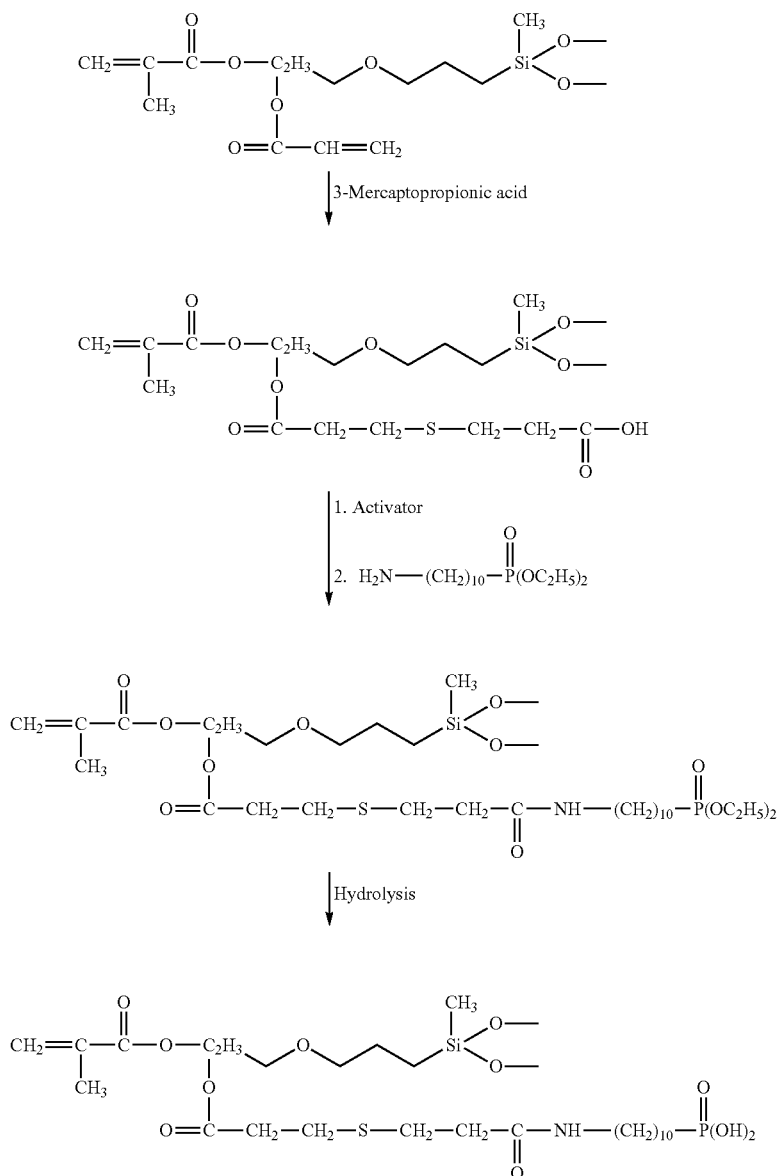
wherein Y' is defined either as Y for the compound (II) or, in the case of Z equal to COOH, an ester or a salt thereof, can instead have the meaning of NHR⁴, NH₂, or OH with R⁴ equal to a non-substituted or substituted hydrocarbon, in particular alkyl or aryl, and in the case of Z equal to OH, can have the meaning of COOH, an ester or a salt thereof, W is defined as for the compound (II) and Q is OH, NR⁷₂, NR⁷₃⁺, CO₂H, SO₃H, PO(OH)₂, PO(OR⁴)₂, OPO(OH)₂, OPO(OR⁴)₂ or a salt of the aforementioned acids, or wherein Y' and Q together form the group —C(O)O(O)C— and W is a straight-chain, branched or cyclical alkylene or alkenylene group with preferably 2 to 12 carbon atoms or a arylene group with preferably 6 to 12 carbon atoms (thus the compound is an anhydride). c represents 1, 2, 3 or 4 or a higher whole number. R⁷ can have the same meaning as R⁴. In addition to this meaning, together two R⁷ radicals can also represent a double-bonded, potentially randomly substituted, potentially unsaturated (even aromatic) hydrocarbon group; accordingly NR⁷₂ and NR⁷₃⁺ can, e.g. be a pyridine radical or the radical of a cyclical ammonium compound or a pyridinium derivative or the like. Radicals Q with the meaning of NR⁷₂ or NR⁷₃⁺ can have essential additional functions in a resin produced pursuant to the invention. Thus, in the case of Z, an activator molecule arises from NR⁷₂, which can be used for a redox-hardening as discussed above. Compounds or resins with NR⁷₃⁺ radicals demonstrate an antimicrobial effect.

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Reactions of aminosulfonic acids, such as 2-Aminoethanesulfonic acid, are principally known and described, e.g. in the registration DE 10 2011 050 672.1 (not yet published on the filing date of the present registration).

If the radical R^2 is an unsaturated, organically polymerizable radical or COOH and Y' is NHR^4 or NH_2 , naturally we cannot preclude in some cases, depending on the reaction conditions, that the amino group of compound (III) will connect to R^2 as well. In those cases, we obtain mixtures that are likewise encompassed by the invention.

A first example for the second variation of the second reaction—in this case in combination with the first reaction—is shown as follows:



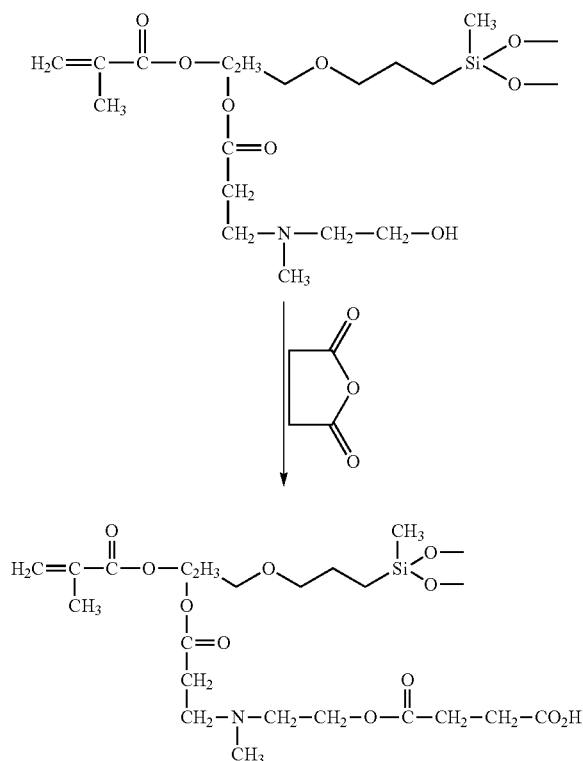
Based on a structure of formula (1), wherein R^1 and R^2 are respectively an unsaturated, organically polymerizable group, in this case an acrylate and a methacrylate group, and m and n are respectively 1, first a structure with the formula

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(2) is produced by reacting with mercaptopropionic acid (compound of the formula (I) with $X=\text{SH}$, $Z=\text{COOH}$ and $a=1$), wherein the linkage group is $A=\text{S}$. This forms in particular when using a (maximum) of one mol of mercaptopropionic acid per mol of silane due to the fact that the addition of SH preferably passes onto the acrylate group. As a result, the formation of the above product is benefited. This product is then converted with a compound with the formula (III), wherein Y' is NH_2 and Q is $-\text{P}(\text{O})(\text{C}_2\text{H}_5)_2$. A structure of a formula (4) emerges, wherein the linkage group B is an acid amide group. The group Q can be transformed into $-\text{P}(\text{O})(\text{OH})_2$ therein through hydrolysis.

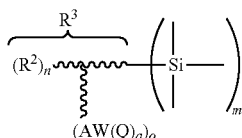
A second example for this reaction is presented based on the reaction with a compound (III), wherein Y' and Q together form the group $-\text{C}(\text{O})\text{O}(\text{O})\text{C}-$ and W is an ethylene group (i.e. with succinic acid anhydride):

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A structure of the formula (4) emerges with a linkage group $A=NR^4$ with $R^4=CH_3$ and a linkage group $B=OC(O)$ (an ester group). The extended chain carries a free carboxylic acid group on its end, which originated from the succinic acid anhydride. In the process, it is necessary to point out that this reaction cannot be depicted entirely properly with the above reaction equation $(2)+(III)\rightarrow(4)$, for Q in (III) is not identical to Q in (4) in this case.

According to the third variation of the second reaction, the product of the first reaction, wherein Z is equal to OH , is converted with phosphorus pentoxide (P_2O_5) or phosphoryl chloride ($POCl_3$). A product with the formula (9) emerges:



wherein Q represents $-O-P(O)(OH)_2$, while all other radicals and indices are defined as in formula (2).

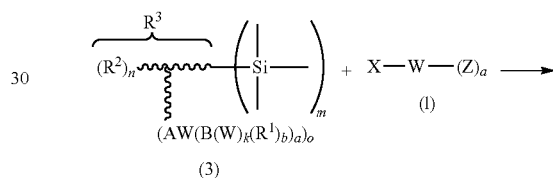
The product (4) of the second variation of the second reaction can be the final product of this embodiment of the invention; with respect to the number of radicals R^1 in the output material, the a -fold number of reactive groups Q multiplied with c that are at a distance from the silicon atom, which is shifted outward by $A-W-B-W$ with respect to the original radical R^1 , can be found therein. The product (9) of the third variation corresponds to product (4) in the event

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that Q represents $-O-P(O)(OH)_2$ with the modification that Q is shifted outward only by $-A-W-$ with respect to the original radical R^1 . The properties that arise through the connection of this functional radical were in part already explained above. Additional advantages are that in product (4), the functional groups are situated far out in the molecule relative to the silicon and, due to the long chains, can move well. This is important for possible additional effects such as the antibacterial effect or the complexation or bonding properties of, e.g. carboxylic acid, phosphorous acid or phosphoric acid groups, which have been vastly improved due to the external location of the respective groups (e.g. forming several effective "connection points").

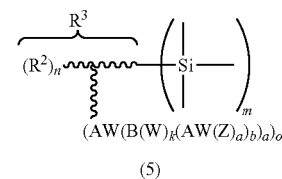
As already explained above, the product (3), which was developed pursuant to the first variation of the second reaction, can be subjected to an additional reaction or an additional cycle of reactions. The next, namely the third reaction, can then occur in two variations:

In the first variation, the product (3) is converted analogously to the first reaction with a compound of formula (I), wherein the radicals and indices have the aforementioned meaning:



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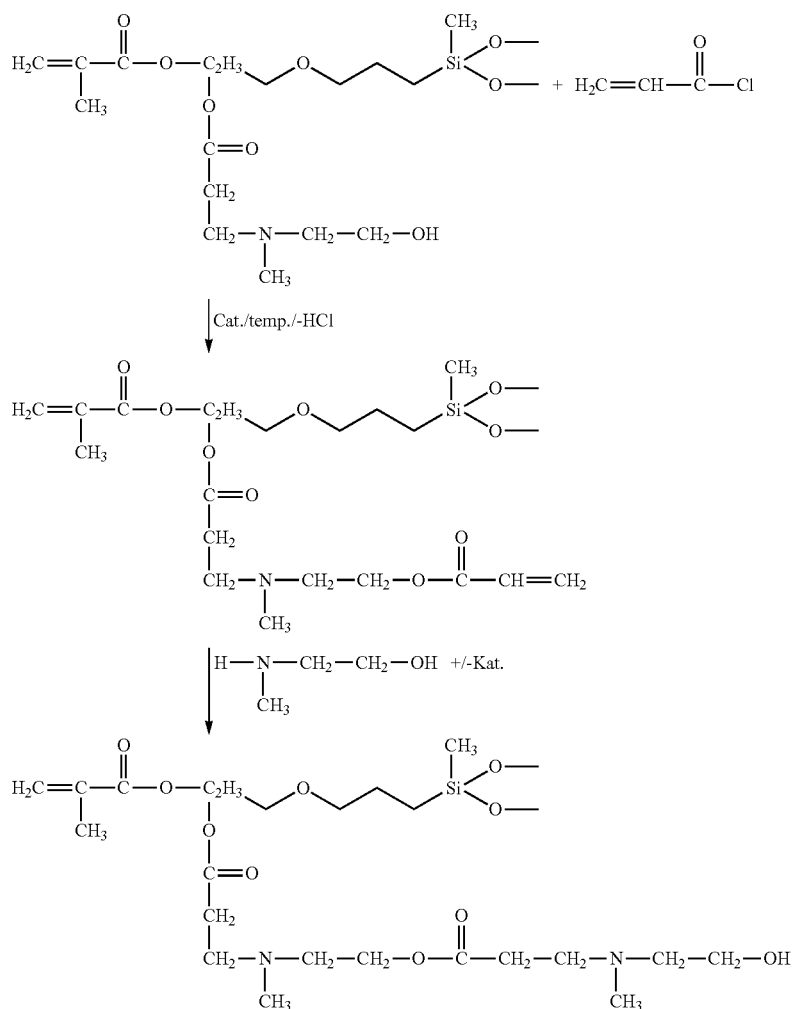


A product emerges, in which the radical Z is present several times on the $Si-C$ -bonded radical, which corresponds to the a^2b -fold of o ; in other words, in lieu of the originally present radical R^1 or each of the originally present radicals R^1 in the output material (1), there are a b radicals Z in the structure (5). If, for example, a dihydroxy compound was used as a compound with the formula (I), as shown in the above examples, while a (mono)methacrylate was used as compound (II), the product (5) contains four organically polymerizable radicals containing double bonds in lieu of each original radical R^1 on an $Si-C$ -bonded radical (the number of which corresponds to index c). If the compound with the formula (I) only contains one hydroxy group, it is only that type of radical. The same applies for the case that the index b in the compound (II) is greater than 1. The emergence of dendrimer-like structures is evident. The radicals Z are shifted outward beyond that with respect to the output material (1) by the group $A-W-B-W-A-W$.

One example for the first variation of the third reaction is shown below:

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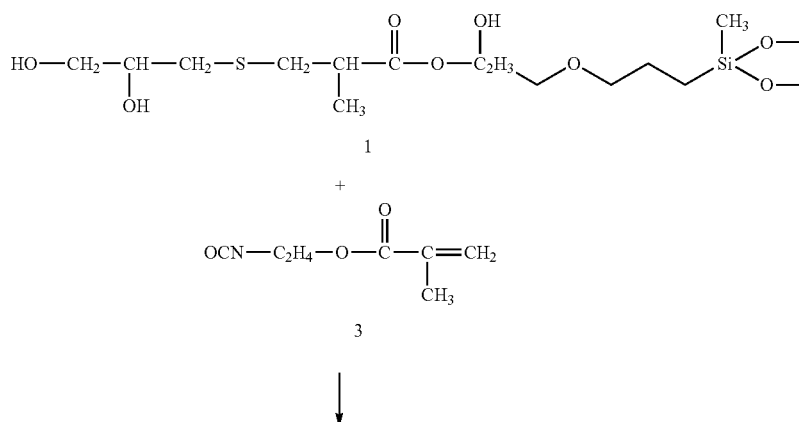
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Based on the product of the above shown third example of the first reaction, a structure (3) with $A=NR^4$, $R^4=CH_3$, $B=$ ester group is formed through a reaction with a compound (II), wherein $Y=COA'$, in this case with $A'=chloride$, $R^1=vinyl$, $b=1$ and $k=0$ (a and o are likewise respectively 1 in this case). This is then converted with a compound of the formula (I), wherein $X=NHR^4$ with $R^4=CH_3$, $Z=OH$ and $a=1$. A structure (5) emerges, in which the second linkage group A

is then NR^4 with $\text{R}^4=\text{CH}_3$. The other groups, radicals, and indices arise from the above explanations to the reactions and compounds. This is identified as structure (5-1).

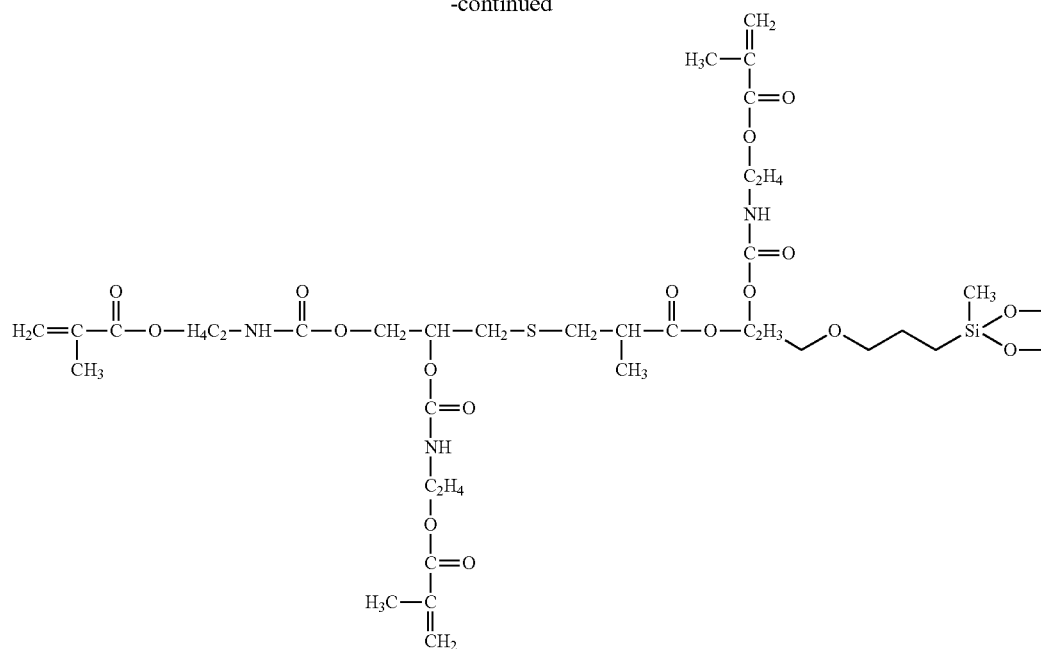
If we instead assume the above explained structure (3-2), which was achieved with 3 equivalents compound (II) in the second reaction through the reaction of a structure (2), which contains three hydroxy groups:



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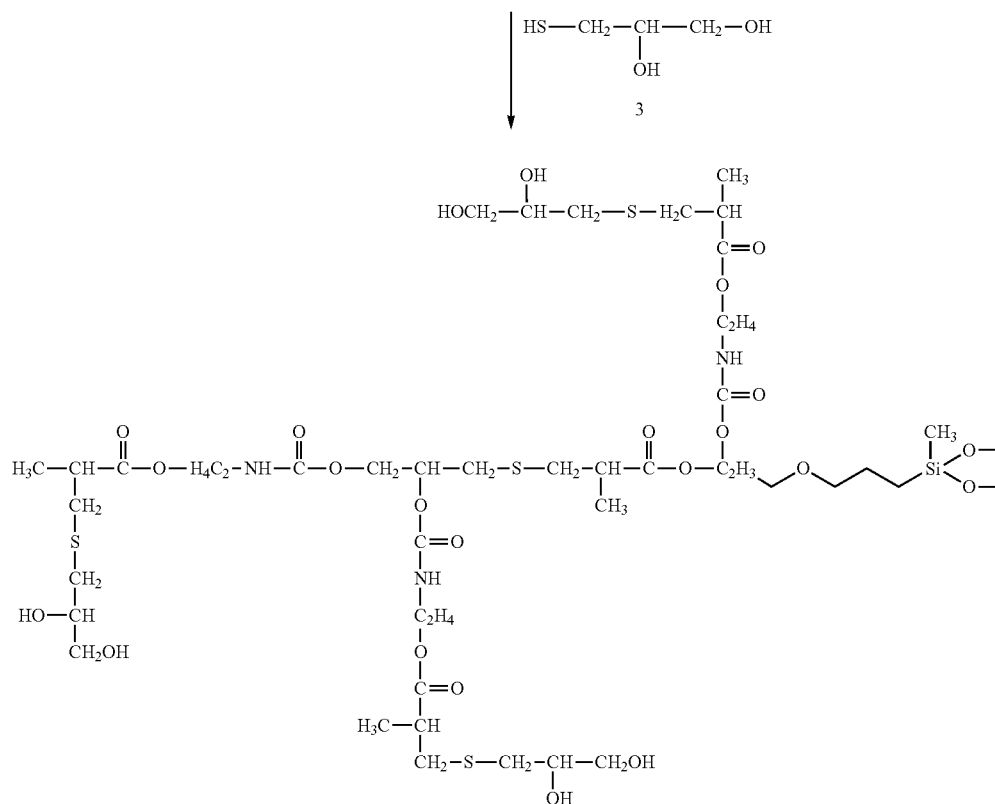
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and convert them with an amount of compound (I)³⁰ equimolar to the radicals R¹, we will obtain a dendrimer-like structure of formula (5), identified in this case as (5-2) (we see that the reactive groups Z arising in the

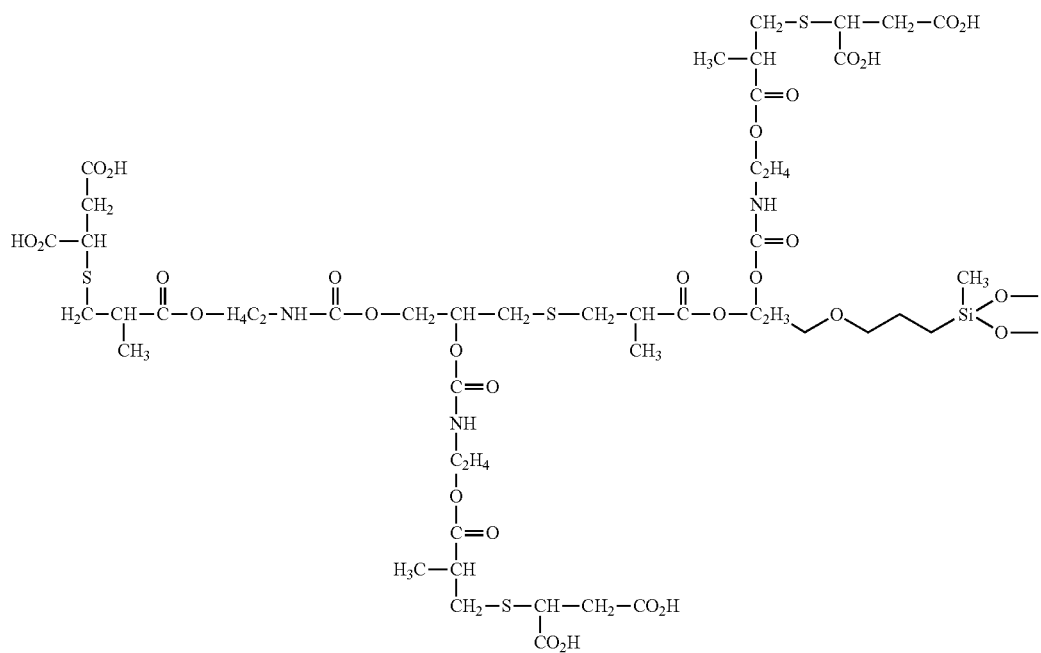
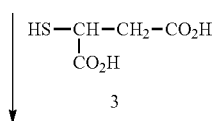
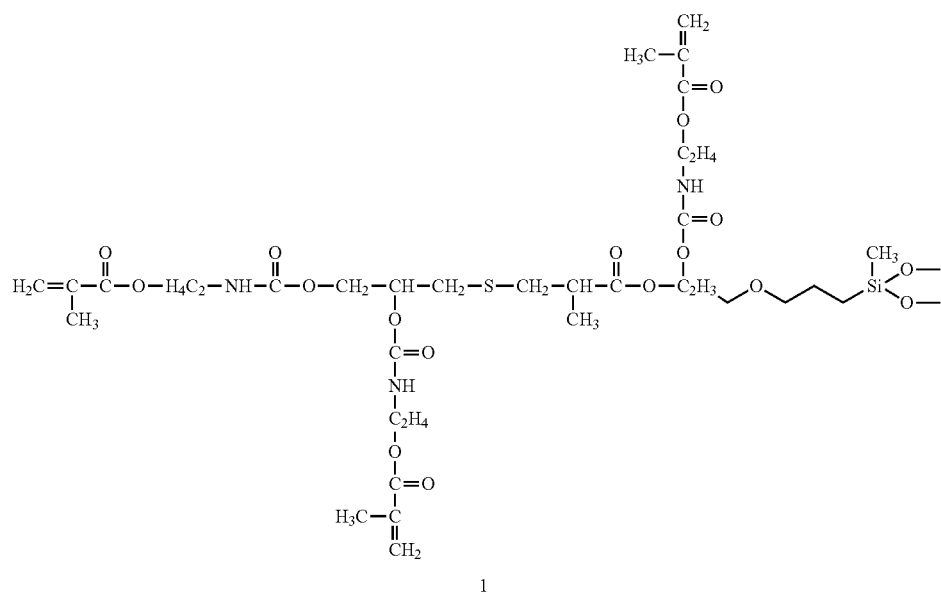
process, namely hydroxy groups, which hang far out on three lateral chains of the Si—C-bonded radical respectively in pairs and, thus, form a dendrimer-like structure):



One example, which, as previously shown, is based on a structure (3) with three groups containing double bonds located far away from each other, is depicted in the following. In this example, X is an SH group in the compound (IV), Q represents a carboxylic acid group, and W represents a hydrocarbon group containing 2 C-atoms. In this formula, c represents 2:

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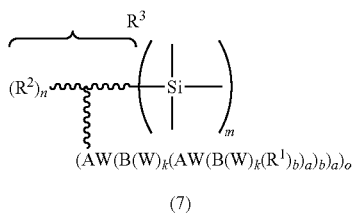
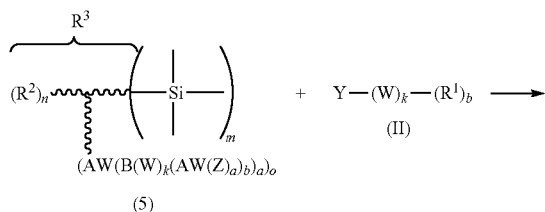
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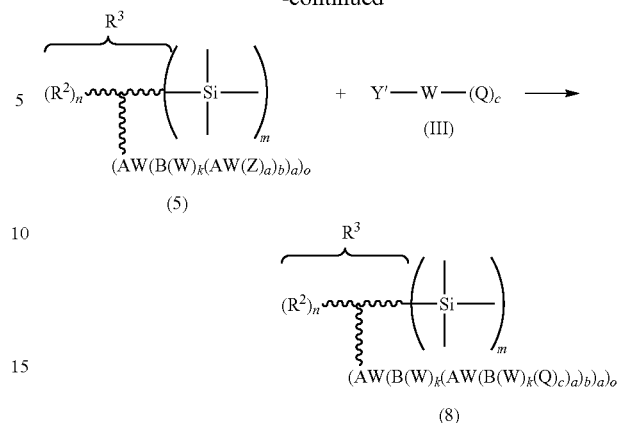
This structure (identified as 6-1) is similar to the structure (5-2) above, although in lieu of the six reactive groups $Z=OH$, it contains six $COOH$ groups.

The product (5) of the first variation of the third reaction in turn can for its part be subjected to a fourth reaction in variations, namely again with a compound with the formula (II) or the formula (III). The products can be depicted as follows, wherein the radicals and indices have the aforementioned meaning:



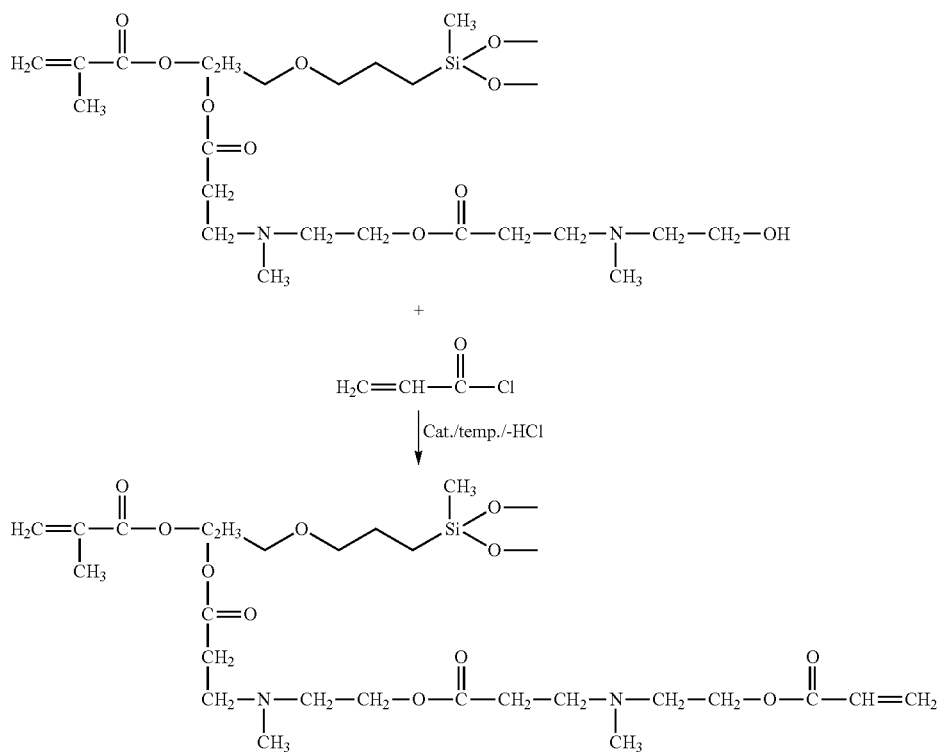
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The products emerging in the process are respectively
comparable with the products from both variations of the
third reaction, wherein the number of radicals R^1 , however, is
present b-fold, the number of radicals Q, however, is present
a-fold with respect to the products (5) and (6), namely with a
once again increased distance to the Si atom. The advantages
correspond accordingly to the descriptions for products (3)
and (4), although they are once again increased. Accordingly,
the radicals R^2 in (7) and (8) represent $B(W)_k(AW(B(W)_k$
 $(R^1)_{b,a})_b$ or $B(W)_k(AW(B(W)_k(Q)_{c,a})_b$.

30 One example for the extension of the structure (5) pursuant to the first variation of the fourth reaction with a compound of the formula (II) through the emergence of the structure (7) is shown below; it is based on the product of the first variation of the third reaction (5-1), the production of which was demonstrated with examples:



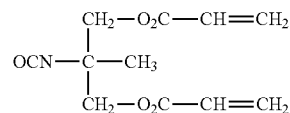
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The reaction occurs in turn with a compound (II) with $Y=COA'$ with A' =chloride, R^1 =vinyl, $b=1$ and $k=0$. Accordingly, the product (7) contains two linkage groups $A=NR^4$ with $R^4=CH_3$ as well as two linkage groups B =ester group.

However, as an output material (5) if we use one with structures that contain a higher number of reactive groups Z , e.g. the above shown structure (5-2) with 6 hydroxy groups, this reaction will produce a product with a structure (7) (structure (7-1)) with a respectively high number (namely 6) of radicals R^1 containing double bonds, wherein the radicals containing double bonds arranged in pairs, in this case methacrylate groups, now have a significant distance to each other as well:

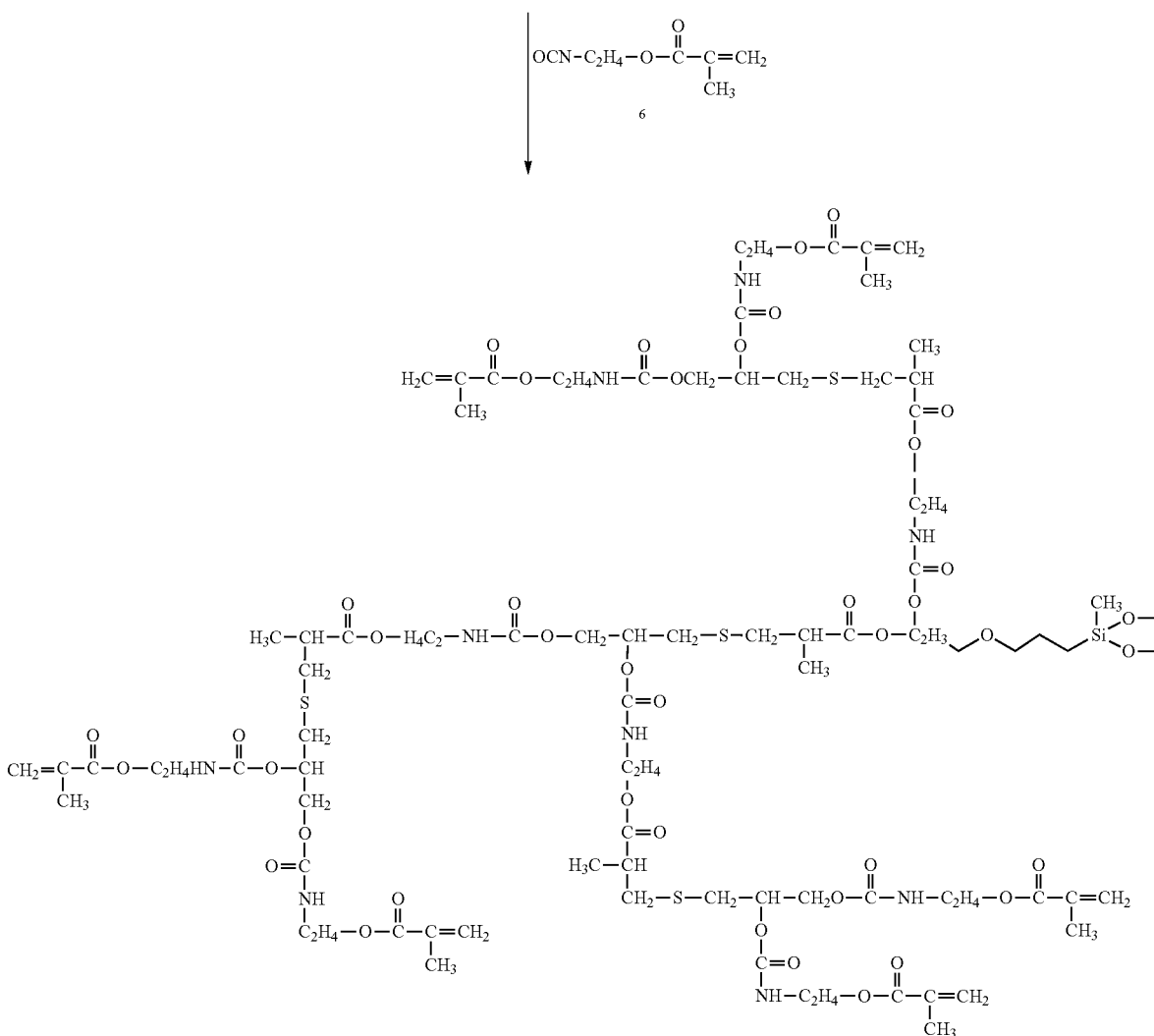
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One example for a comparable reaction of (5) with (II) pursuant to (7) is the reaction of structure (5-3) with the following compound (II):



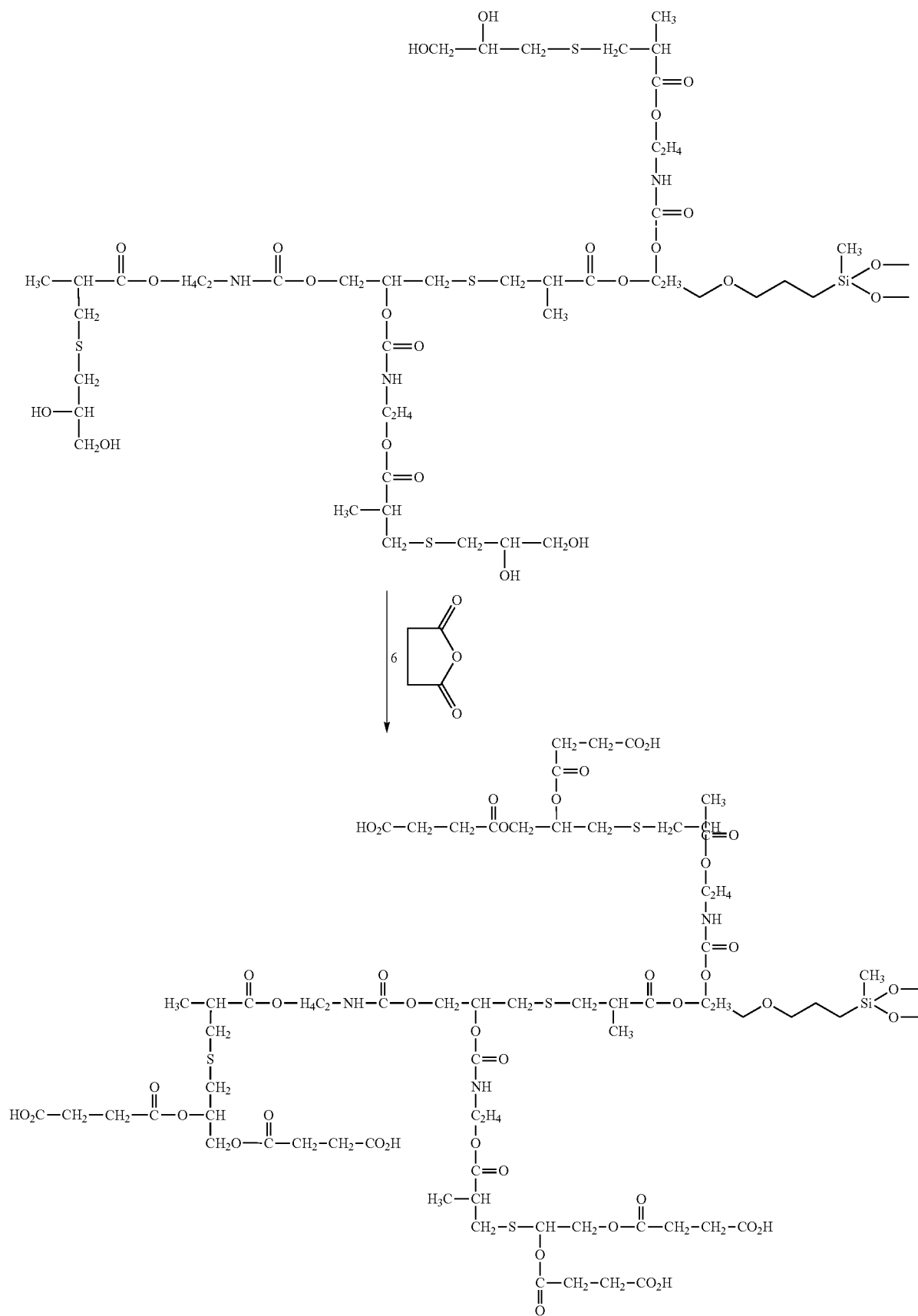
The product has the structure (7) and has 12 double bonded groups (structure (7-2)).

Based on (5-2), with the reaction with a molecule (III), we achieve a structure (8) with 6 carboxylic acid groups that are comparably arranged:



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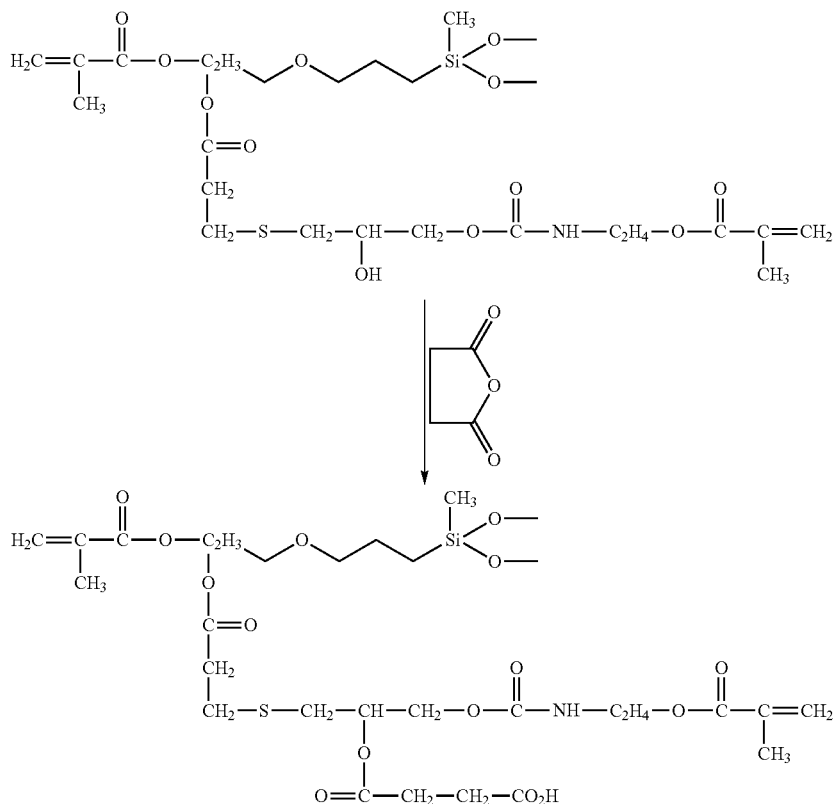
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The principle of the reaction sequence can fundamentally be continued; due to the fact that the products—at least in those cases, in which X is equal to SH or Y is equal to NCO, and particularly then if the compounds (I) to (IV) are used in the deficit with regard to the respectively convertible radicals—do not have to be isolated or purified, structures with any number of reactive groups Q located far out or organically polymerizable radicals R^1 can be produced on respectively one Si—C-bonded radical, which are potentially branched out like a dendrimer.

If the products of a structure (3) have free, reactive groups Z, e.g. OH groups because, for instance the initial reaction occurred with compound (I), in which a >1 and the subsequent reaction of a product (2) occurred with compound (II) in the deficit, an alternative to another a reaction with a compound of formula (I) and then potentially with formula (II) is another reaction of these groups. A compound must be used to achieve this, which reacts with Z, though not with R^1 . For the event that the free groups Z are hydroxy groups, an anhydride, for example, can be used for this, as the following example demonstrates:



Instead, this additional reaction with a compound (V) can be conducted with a formula $\text{Y}''\text{W}(\text{Q})_c$, wherein Y'' represents NCO, epoxy or COA' with $\text{A}'=\text{hydroxy}$, a halogenide or $-\text{OC}(\text{O})\text{R}^4$ with $\text{R}^4=\text{non-substituted or substituted hydrocarbon radical}$ and W, Q, and c are defined above as for compound (III).

Together with this reaction, a reactive group is in turn likewise shifted to a spot further out in the molecule, wherein, however, the group R^1 remains untouched.

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The silicic acid polycondensates pursuant to the invention can be hardened in various manners. Thus, the existing $\text{C}=\text{C}$ double bonds can be introduced to a cross-linking through a polyaddition with thiols and amines or a polymerization reaction through the formation of propagating carbon chains, which causes the material to harden. The condensates can also be hardened by other cross-linking reactions, e.g. through a reaction with di-, tri- or tetra-isocyanates, which connect to free carboxylic acid or hydroxy groups, or respectively multifunctional anhydrides for the reaction of condensates containing hydroxy groups, through which another, purely organic cross-link also arises.

The resin systems (i.e. the silicic acid polycondensates) of the present invention or their hardened products can be used for a number of applications, including in particular dental purposes, preferably for direct/indirect restorations, prophylaxis (e.g. through fissure sealing), prosthetics, and tooth replacement.

In the following, the invention is explained in further detail based on specific examples of reactions:

Example 1

Synthesis of the Base Resin System I (State of the Art)

For receiving 125.0 g (0.503 mol) of 3-Glycidyloxypropyltrimethoxysilane, triphenylphosphine (as a cat.), BHT (as a stabilizer), and then 47.35 g (0.550 mol) of methacrylic acid are added drop-wise in a dry atmosphere and stirred at 80° C. (approx. 24 hrs.). The reaction can be traced by the decline in carboxylic acid concentration via acid titration as well as the epoxy conversion via a Raman spectroscopy/epoxy titration.

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The band of epoxy silane characteristic for the epoxy group appears in the Raman spectrum at 1256 cm^{-1} . The epoxy or carboxylic acid conversion is at $\geq 99\%$ or $\geq 89\%$ (\rightarrow due to 1:1.1 carboxylic acid surplus). After adding acetic ester (1000 ml/mol of silane) and H_2O for hydrolysis with HCl as cat., stir at 30°C . The progress of hydrolysis is respectively followed via water titration. Processing occurs after approx. multiple days of stirring through repeated extraction with aqueous NaOH and with water and filtration via hydrophobized filters. A rotary evaporator is used first and then an oil pump vacuum is used for suctioning. This resulted in a liquid resin without the use of reactive thinners (monomers) with a very low viscosity of approx. 3-6 Pa·s at 25°C . (heavily dependent upon exact hydrolysis and processing conditions) and 0.00 mmol of $\text{CO}_2\text{H/g}$ (no free carboxyl groups) as well as a refractive index n_D of approx. 1.480.

Example 1a

For receiving 48.3 g (0.18 mol) from Base Resin System I and potentially 0.10 g of triethylamine, 5.50 g (0.051 mol) of thioglycerol (3-Mercaptopropan-1,2-diol) are added drop-wise while stirring. The reaction can be followed via NMR as well as through the decline of the HS bonds via Raman spectroscopy. The band characteristic for the HS group appears in the Raman spectrum at 2566 cm^{-1} . The result is a liquid resin with a viscosity of approx. 16-18 Pa·s at 25°C . (dependent upon the exact synthesis and processing conditions of the preliminary stages) and a refractive index n_D of approx. 1.489. Additional processing is normally not necessary. The molar ratio of the deployed Base Resin System I to the product of the reaction with thioglycerol in the achieved resin is 1:0.282.

Example 1b

For receiving 37.2 g (0.14 mol) from Base Resin System I and potentially 0.16 g of a triethylamine, 8.54 g (0.079 mol) of thioglycerol (3-Mercaptopropan-1,2-diol) are added drop-wise while stirring. The result is a liquid resin with a viscosity of approx. 39 Pa·s at 25°C . and a refractive index n_D of approx. 1.497. Additional processing is normally not necessary (see note for Example 2a). The molar ratio of the deployed Base Resin System I to the product of the reaction with thioglycerol in the achieved resin is 1:0.56.

The refractive index of this product can be finely adjusted through the share of thiol (see slight increase with respect to Base Resin System 1)

The polarity/hydrophilicity is adjustable through the OH content, which is introduced by the thiol compound as in this case via thioglycerol (i.e. heavy, graded increase compared to Base Resin System 1)

Example 2a

For receiving 13.09 g (0.040 mol) of a resin from example 1b and potentially 0.028 g of BHT, 3.48 g (0.0224 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30°C . and continually stirred at 30°C . The reaction can be followed through the decline of the OCN band via the IR spectrum. The band characteristic for the OCN group appears in the IR spectrum at 2272 cm^{-1} . The result is a liquid resin with a viscosity of approx. 85 Pa·s at 25°C . (heavily dependent upon the exact synthesis and processing conditions, particularly the preliminary stages).

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Example 2b

For receiving 13.09 g (0.040 mol) of a resin from example 1b and potentially 0.035 g of BHT, 6.59 g (0.0448 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30°C . and continually stirred at 30°C . The result is a liquid resin with a viscosity of approx. 207 Pa·s at 25°C . (see note for 2a)

Example 2c

For receiving 9.82 g (0.030 mol) of a resin from example 1b and potentially 0.030 g BHT, 7.08 g (0.0456 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30°C . and continually stirred at 30°C . The result is a liquid resin with a viscosity of approx. 207 Pa·s at 25°C . (see note for 2a).

Example 2d

For receiving 14.87 g (0.050 mol) of a resin from example 1a and potentially 0.030 g of BHT, 4.38 g (0.0282 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30°C . and continually stirred at 30°C . The result is a liquid resin with a viscosity of approx. 43 Pa·s at 25°C . (see note for 2a).

Example 2e

For receiving 14.87 g (0.050 mol) of a resin from example 1a and potentially 0.040 g of BHT, 9.81 g (0.0632 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30°C . and continually stirred at 30°C . The result is a liquid resin with a viscosity of approx. 167 Pa·s at 25°C . (see note for 2a).

Example 3

For receiving 20.81 g (0.070 mol) of a resin from example 1a, 16.83 g (0.109 mol) of methacrylic acid anhydride are added drop-wise while stirring in a dry atmosphere at 65°C . and continually stirred at 65°C . The reaction can be followed via NMR and the decline of the anhydride band can be followed via IR spectrum. The band characteristic for the anhydride group appears in the IR spectrum at $1785/1722\text{ cm}^{-1}$. Following the usual processing for separating the methacrylic acid released during the addition as well as the extraction of the volatile components with the oil pump vacuum, a liquid resin emerges with a viscosity of approx. 8 Pa·s at 25°C . (heavily dependent upon the exact synthesis and processing conditions, particularly the preliminary stages).

TABLE 1

Resin system	Breaking strength [MPa]	Modulus of elasticity [GPa]	Deflection [mm]	Contraction (15 min./1 day) [Vol.-%]
Base resin system I (comparison)	83	1.5	2.9	5.2/5.8
2b	120	2.60	3.20	
2c	127	2.82	2.60	
2d	107	2.30	3.26	
2e	136	2.85	2.92	4.8/5.8
2f	138	3.07	2.14	
3	103	2.32	2.35	

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Example 4

For receiving 20.81 g (0.070 mol) of a resin from example 1a and 5.45 g of triethylamine (0.0501 mol) in 70 ml of THF as a solvent, 5.12 g (0.0455 mol) of methacrylic acid chloride are added drop-wise in a dry atmosphere and through cooling in an ice bath and continually stirred at room temperature. The reaction can be followed via NMR and the decline of the acid chloride band can be followed via IR spectrum. Following the usual processing for separating the amine hydrochloride produced during the addition as well as the extraction of the volatile components with an oil pump vacuum, a liquid resin emerges with a viscosity of approx. 6.9 Pa·s at 25° C.

Example 5

Synthesis of Base Resin System II (State of the Art)

For receiving 120.1 g (0.45 mol) from Base Resin System I (Example 1) and 35.1 g of triethylamine (0.347 mol) in 450 ml of THF as a solvent, 28.51 g (0.315 mol) of acrylic acid chloride are added drop-wise in a dry atmosphere and through cooling in an ice bath and continually stirred at room temperature. The reaction can be followed via NMR and the decline of the acid chloride band can be followed via IR spectrum. Following the usual processing for separating the amine hydrochloride produced during the addition as well as the extraction of the volatile components with an oil pump vacuum, a liquid resin emerges with a viscosity of approx. 1.5 Pa·s at 25° C. (heavily dependent upon the exact synthesis and processing conditions, particularly the preliminary stages).

Example 5a

For receiving 39.13 g (0.13 mol) from Base Resin System II and potentially 0.17 g of triethylamine, 9.00 g (0.0832 mol) of thioglycerol (3-Mercaptopropan-1,2-diol) are added. The reaction can be followed via NMR as well as through the decline of the HS bonds via Raman spectroscopy. The band characteristic for the HS group appears in the Raman spectrum at 2566 cm⁻¹. The result is a liquid resin with a viscosity of approx. 23 Pa·s at 25° C. (dependent upon the exact synthesis and processing conditions, particularly the preliminary stages). Additional processing is normally not necessary.

Example 6a

For receiving 16.47 g (0.045 mol) of a resin from example 5a (molar ratio=1:0.6) and potentially 0.021 g of BHT, 4.19 g (0.027 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30° C. and continually stirred at 30° C. The reaction can be followed through the decline of the OCN band via the IR spectrum. The band characteristic for the OCN group appears in the IR spectrum at 2272 cm⁻¹. The result is a liquid resin with a viscosity of approx. 62 Pa·s at 25° C. (heavily dependent upon the exact synthesis and processing conditions, particularly the preliminary stages). Additional processing is normally not necessary.

Example 6b

For receiving 16.47 g (0.045 mol) of a resin from example 5a (molar ratio=1:0.6) and potentially 0.030 g of BHT, 8.38 g (0.054 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30° C.

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and continually stirred at 30° C. The result is a liquid resin with a viscosity of approx. 164 Pa·s at 25° C. (see note for 6a).

TABLE 2

Resin system	Breaking strength [MPa]	Modulus of elasticity [GPa]	Deflection [mm]
Base resin system II (comparison)	79	1.74	1.98
After the addition of thiol → Drastic increase of OH content			
5a	48	0.91	2.70
After the addition of isocyanate methacrylate			
6a	122	2.53	2.90
6b	132	2.95	2.40

Example 7a

For receiving 36.04 g (0.12 mol) from Base Resin System II, 5.41 g (0.072 mol) of 2-Methylamino-ethanol are slowly (exothermal reaction) added while stirring. The reaction can be followed via NMR. The result is a liquid resin with a viscosity of approx. 5 Pa·s at 25° C. (dependent upon the exact synthesis and processing conditions, particularly the preliminary stages). Additional processing is normally not necessary.

Example 8a

For receiving 12.44 g (0.036 mol) of resin from example 7a (molar ratio=1:0.5) and potentially 0.031 g of BHT, 2.79 g (0.018 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30° C. and continually stirred at 30° C. The reaction can be followed through the decline of the OCN band via the IR spectrum. The band characteristic for the OCN group appears in the IR spectrum at 2272 cm⁻¹. The result is a liquid resin with a viscosity of approx. 15 Pa·s at 25° C. (heavily dependent upon the exact synthesis and processing conditions, particularly the preliminary stages). Additional processing is normally not necessary.

Example 8b

For receiving 11.74 g (0.034 mol) of resin from example 7a (molar ratio=1:0.7) and potentially 0.031 g of BHT, 3.69 g (0.0238 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30° C. and continually stirred at 30° C. The result is a liquid resin with a viscosity of approx. 20 Pa·s at 25° C. Additional processing is normally not necessary (see note for 8a).

Example 8c

For receiving 5.00 g (0.0145 mol) of resin from example 7a (molar ratio=1:0.9) and potentially 0.014 g of BHT, 2.02 g (0.0130 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30° C. and continually stirred at 30° C. The result is a liquid resin. Additional processing is normally not necessary (see note for 8a).

Example 9a

For receiving 60.1 g (0.20 mol) from Base Resin System II, 10.5 g (0.10 mol) of diethanolamine are slowly (exothermal

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reaction) added drop-wise while stirring. The reaction can be followed via NMR. The result is a liquid resin with a viscosity of approx. 9-12 Pa·s at 25° C. (dependent upon the exact synthesis and processing conditions, particularly the preliminary stages). Additional processing is normally not necessary. With 3.8/4.2 Vol.-% (15 min./1 day), the monomer-free resin system demonstrates a surprisingly low level of hardening shrinkage.

Example 10a

For receiving 10.59 g (0.030 mol) of resin from Example 9a and potentially 0.029 g of BHT, 3.72 g (0.024 mol) of methacrylic acid isocyanatoethyl ester are added drop-wise while stirring in a dry atmosphere at 30° C. and continually stirred at 30° C. The reaction can be followed through the decline of the OCN band via the IR spectrum. The band characteristic for the OCN group appears in the IR spectrum at 2272 cm⁻¹. The result is a liquid resin with a viscosity of approx. 39-45 Pa·s at 25° C. (heavily dependent upon the exact synthesis and processing conditions, particularly the preliminary stages). Additional processing is normally not necessary. With 4.0/4.8 Vol.-% (15 min./1 day), the monomer-free resin system demonstrates a surprisingly low level of hardening shrinkage.

Determination of the mechanical data as well as the hardening shrinkage:

Polymerization/hardening of various resin systems compared to the fundamental base resins:

The respective resin from the series of examples or the base resin systems 1/2 with % Lucirin TPO is added to a rod shape (2×2×25 mm³). The (meth)acrylate groups are converted within the scope of a photo-induced radical polymerization, wherein the resin hardens. Using a 3-point bending test, the modulus of elasticity, the breaking strength, and deflection to the point of breakage of the resulting rods is determined after 1.5 days in storage at 40° C.

The shrinkage values are obtained using the buoyancy method within the scope of the photo-induced radical polymerization (15 min./1 day after exposure).

The examples allows us to see that, in a single materials base, a generally very broad spectrum of the modulus of elasticity is adjustable and clearly improved mechanical data (increased strength) is observed compared to the underlying base resin (state of the art). The systems can be implemented without the use of dental monomers, which is essential in light of increasing discussions about allergies in the dental field. The invention enables an additional functionality through the introduction of additional OH, or other groups. The products achieved in this manner have a surprisingly low shrinkage value.

What is claimed is:

1. A process for a chain extension of Si—C bonded radicals of silanes or siloxanes having at least two functional groups, wherein the number of functional groups on the respective Si—C bonded radicals is maintained or increased,

wherein

a silane or siloxane with a radical bonded to a silicon atom by a carbon atom, the radical bearing at least two functional groups,

wherein a first group of the functional groups is an unsaturated, organically polymerizable group and a second group of said functional groups is selected among

(a) additional unsaturated, organically polymerizable groups,

(b) COOR⁸ or —(O)_bP(O)(R⁵)₂ and

(c) —OH,

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with R⁸ equal to R⁴ or M_{1/x}^{x+}, M^{x+} being hydrogen or an x-fold positively charged metal cation, and b=0 or 1, is converted in an initial reaction with a compound of a formula (I)



wherein

X is SH, NH₂ or NHR⁴,

Z is OH, a carboxylic acid group —COOH or a salt or an ester of said group or a silyl group having formula SiX*₃, wherein the radicals X* represent a hydrocarbon radical, W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by

—S—, —O—, —NH—, —NR⁴—, —C(O)O—, —NHC(O)—, —C(O)NH—, —NHC(O)O—, —C(O)NHC(O)—, —NHC(O)NH—, —S(O)—, —C(S)O—, —C(S)NH—, —NHC(S)—, —NHC(S)O—, and

a represents 1, 2, 3, 4 or a greater whole number, and wherein

R⁴ is a non-substituted or substituted hydrocarbon group,

R⁵ is a non-substituted or substituted hydrocarbon group or OR⁶, and

R⁶ is hydrogen or is a non-substituted or substituted hydrocarbon group, such that the group X reacts with the first functional group.

2. Process according to claim 1, wherein Z is OH, the carboxylic acid group

—COOH or a salt or an ester of said group.

3. Process according to claim 2, wherein the second of the functional groups of the radical bonded to a silicon atom of the silane or siloxane is an OH group.

4. Process according to claim 2, wherein the index a in the compound with said formula (I) represents 2, 3 or 4, and particularly 2.

5. Process according to claim 2, wherein X is SH, Z is OH, and a represents 2 or 3 in the compound with said formula (I).

6. Process according to claim 1, wherein a molar ratio of the first or all groups on the functional groups on the Si—C bonded radicals to the groups Z in the compound with said formula (I) is >1 to 1, preferably being at least 1.05 to 1, and even more preferred being in the range of 1.05 to 1 to 1.50 to 1.

7. Process according to claim 2, wherein the product of said process is further reacted in a second reaction with a compound (II)



wherein Y is NCO, epoxy or, if the group or groups Z in the product of said process is/are (a) hydroxy group(s), COA',

W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by

—S—, —O—, —NH—, —NR⁴—, —C(O)O—, —NHC(O)—, —C(O)NH—, —NHC(O)O—, —C(O)NHC(O)—, —NHC(O)NH—, —S(O)—, —C(S)O—, —C(S)NH—, —NHC(S)—, —NHC(S)O—,

R¹ is an unsaturated, organically polymerizable group,

A' is hydroxy, a halogenide or —OC(O)R⁴ with R⁴ being a non-substituted or substituted carbon group,

k=0 or 1, wherein k=0 is only possible in the event that Y represents COA', and

b=1 or greater than 1,

wherein the molar ratio of the product of the first reaction to the compound with formula (II) is preferably greater than 1, and more preferred being at least 1.05.

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8. Process according to claim 7, wherein said process occurred with said compound (I), for which Z=OH, wherein compound (II) in the second reaction is used substoichiometrically with regard to the groups Z present in the product of the first reaction.

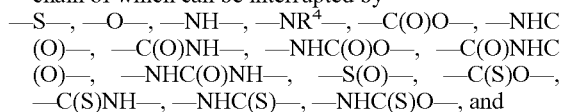
9. Process according to claim 2, wherein the product of said process is further converted in a second reaction, either with a compound (III)



wherein

Y' is either is NCO, epoxy if the group or groups Z in the product of said process is/are (a) hydroxyl group(s), CAO', or, in the case of Z equal to COOH or a salt thereof, can instead have the meaning of NHR⁴, NH₂, or OH with R⁴=non-substituted or substituted hydrocarbon and, in the case of Z equal to OH, can have the meaning of COOH or a salt thereof,

W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by



Q is OH, NR⁷₂, NR⁷₃⁺, CO₂H, SO₃H, PO(OH)₂, PO(OR⁴)₂, OPO(OH)₂, OPO(OR⁴)₂ or a salt of the previously mentioned acids, wherein R⁴ has the above-specified meaning for said formula (I) and R⁷ either has the same meaning as R⁴ or two groups together can represent a potentially substituted or potentially unsaturated alkylene group, and

c is 1, 2, 3, 4 or a greater number, or, wherein

Y' and Q together form a group —C(O)O(O)C— and W is a straight-chain, branched or cyclic alkylene or alkenylene group, preferably with respectively 2 to 12 carbon atoms or an optionally alkyl-substituted or condensed arylene group, preferably with 6 to 12 carbon atoms,

or, in the event that the group or groups Z in the product of the first reaction is/are (a) hydroxy group(s), is converted with P₂O₅ or with POC_l₃,

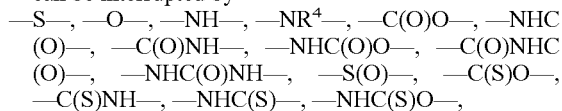
wherein the molar ratio of the product of the first reaction to the compound with formula (III) is preferably greater than 1, and more preferred being at least 1.05.

10. Process according to claim 7, wherein in said compound with the formula (II), Y is COA' and, in particular, is (meth)acrylic acid chloride or anhydride.

11. Process according to claim 7, wherein the product of the second reaction is further reacted in a third reaction with a compound (IV)



wherein X is SH, NH₂ or NHR⁴ and W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by



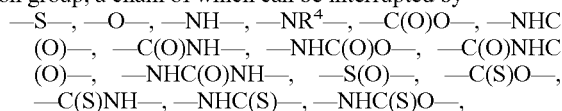
Q is OH, NR⁷₂, NR⁷₃⁺, CO₂H, SO₃H, PO(OH)₂, PO(OR⁴)₂, OPO(OH)₂, OPO(OR⁴)₂ or a salt of the previously mentioned acids, wherein R⁴ has the above-specified meaning for said formula (I) and R⁷ either has the same meaning as R⁴ or two groups R⁷ together can represent a potentially substituted or potentially unsaturated alkylene group, and

c is 1, 2, 3, 4 or a greater number,

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wherein the molar ratio of the product of the second reaction to the compound with the formula (IV) is preferably greater than 1, and more preferred being at least 1.05.

12. Process according to claim 8, further comprising a reaction with a compound (V), which is selected from the group consisting of an anhydride of a dicarboxylic acid and a compound of a formula Y''WC(Q)_c, wherein Y'' has the meaning of NCO, epoxy or COA' with A'=hydroxy, a halogenide or —OC(O)R⁴ with R⁴=a non-substituted or substituted hydrocarbon group, W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by



Q is OH, NR⁷₂, NR⁷₃⁺, CO₂H, SO₃H, PO(OH)₂, PO(OR⁴)₂, OPO(OH)₂, OPO(OR⁴)₂ or a salt of the previously mentioned acids, wherein R has the above-specified meaning for said formula (I) and R⁷ either has the same meaning as R⁴ or two groups R⁷ together can represent a potentially substituted or potentially unsaturated alkylene group, and

c is 1, 2, 3, 4 or a greater number.

13. Process according to claim 7, wherein the product of the second reaction is further converted in a third reaction with a compound of said formula (I):

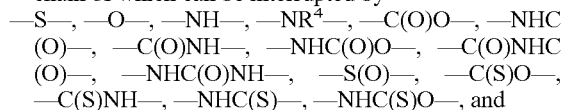


wherein

X is SH, NH₂ or NHR⁴,

Z is OH, a carboxylic acid group —COOH or a salt or an ester of said group or a silyl group,

W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by



a represents 1, 2, 3, 4 or a greater whole number,

wherein

R⁴ is a non-substituted or substituted hydrocarbon group,

R⁵ is a non-substituted or substituted hydrocarbon group or OR⁶, and

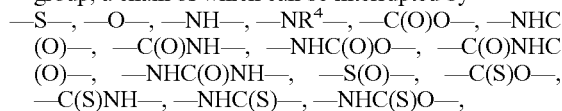
R⁶ is hydrogen or is a non-substituted or substituted hydrocarbon group,

wherein the molar ratio of the product of the second reaction with said formula (I) in the third reaction is greater than 1, and preferably being at least 1.05.

14. Process according to claim 13, wherein the product of the process is further reacted in a fourth reaction either with a compound (III)



wherein Y is NCO, epoxy or if the group or groups Z in the product of the first reaction is/are (a) hydroxy group(s) COA', W is a substituted or non-substituted hydrocarbon group, a chain of which can be interrupted by



Q is OH, NR⁷₂, NR⁷₃⁺, CO₂H, SO₃H, PO(OH)₂, PO(OR⁴)₂ or a salt of the aforementioned acids, wherein R⁴ is a non-substituted or substituted hydrocarbon group, R⁷ either has the same meaning as R⁴ or two groups R⁷ together represent an optionally substituted, optionally unsaturated alkylene group, and c is 1, 2, 3, 4

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or a greater number, wherein the molar ratio of the product of the first reaction to the compound with said formula (II) is preferably greater than 1, and more preferably being at least 1.05, or, in the event that the group or groups Z in the product of the third reaction is/are (a) 5 hydroxy group(s), is converted with P_2O_5 or $POCl_3$.

15. Process according to claim 13, wherein the product of the third reaction is further reacted in a fourth reaction with a compound having the formula (II), wherein the molar ratio of the product of the third reaction to the compound with said formula (II) is preferably greater than 1, and more preferably 10 being at least 1.05.

16. Process according to claim 7, further comprising

(a) the reaction of the respective product with a one or more multifunctional thiol, or

(b) the polymerization of the respective product in a polyreaction, for which a part or all of the available reactive double bonds are integrated under the influence of heat, light, ionizing radiation or redox-induced in a propagating carbon chain. 15

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17. Process according to claim 1, further comprising

(a) the cross-linking of existing hydroxy or carboxylic acid groups with a di- or polyfunctional isocyanate, or

(b) the cross-linking of existing hydroxy groups with a di- or polyfunctional, optionally activated, carboxylic acid.

18. Process according to claim 9, wherein in said compound with the formula (III), Y' is COA' and, in particular, is (meth)acrylic acid chloride or anhydride, or wherein $Y'W(O)_c$ is succinic anhydride, glutaric anhydride or maleic anhydride.

19. Process according to claim 15, further comprising

(a) the reaction of the respective product with a one or more multifunctional thiol, or

(b) the polymerization of the respective product in a polyreaction, for which a part or all of the available reactive double bonds are integrated under the influence of heat, light, ionizing radiation or redox-induced in a propagating carbon chain.

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